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Marine Pollution Monitoring (Petroleum)

Proceedings of a Symposium Sponsored by:

The Intergovernmental Oceanographic Commission (IOC-UNESCO)

The World Meteorological Organization (WMO)

United States Department of Commerce

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Marine Pollution Monitoring (Petroleum)

Proceedings of a Symposium and Workshop
Held at the National Bureau of Standards,
Gaithersburg, Md., May 13-17, 1974

Sponsored by

The Intergovernmental Oceanographic
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The World Meteorological Organization
The U.S. Department of Commerce

t. Special publication no. 409

R. C. Junghans, Conference Coordinator

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ABSTRACT

These proceedings contain the invited plenary lectures representing pertinent scientific, environmental, and regulatory aspects of petroleum hydrocarbon measurements, the summaries of the contributed papers, dealing with specific scientific developments and recommendations, and the recommendations of the topical discussion groups. Also included is a report of an international workshop which provides specific recommendations for the initiation of a coordinated Pilot Project for marine pollution (petroleum) monitoring.

Key Words: Analytical methods; data reporting procedures; Intergovernmental Oceanographic Commission (IOC); marine pollution (petroleum) monitoring; Maritime Administration (MarAd); National Bureau of Standards (NBS); National Oceanic and Atmospheric Administration (NOAA); petroleum hydrocarbon measurement; oil slicks and tar balls; sampling methods; World Meterological Organization (WMO).

FOREWORD

The increasing amount of petroleum being transported over the world's waterways has prompted a good deal of interest in the environmental impact of oil pollution. The need for a comprehensive international marine environmental monitoring assessment program serving both research and operational activities is recognized by the U. S. Department of Commerce. Thus it was proper that three agencies within the Department of Commerce, the Maritime Administration (MarAd), the National Bureau of Standards (NBS), and the National Oceanic and Atmospheric Administration (NOAA) cosponsor and host the Marine Pollution Monitoring (Petroleum) Symposium and Workshop held at NBS in Gaithersburg, May 13-17, 1974.

The publication of the proceedings of this meeting is the joint effort of MarAd, NBS and NOAA. This book contains the invited plenary lectures, the summaries of the contributed papers and the recommendations of the topical discussion groups as well as the Workshop's recommended procedures and methodology for use by National Coordinators in the implementation, at the national level, of the operational programs for the Pilot Project on Marine Pollution Monitoring.

J. D. Hoffman, Director
Institute for Materials Research
National Bureau of Standards

These areas are chosen to be suitable for initiation of the Pilot Project, Integrated Global Oceanic Station System (IGOSS).

PREFACE

The International Symposium and Workshop was prompted by the recognized need to communicate and exchange ideas and results on an international basis, which reflect the status of current methodology for making measurements of petroleum and petroleum products in the marine environment. Such needs arose as the Intergovernmental Oceanographic Commission and the World Meteorological Organization decided to establish an operational Pilot Project for Marine Pollution Monitoring which was initially to focus on petroleum hydrocarbons within the framework of the IGOSS program.

IGOSS, the Integrated Global Ocean Station System, is aimed at evolving a comprehensive international marine environmental monitoring, assessment and prediction program of services to various categories of ocean users--both for research support and for operational activities.

The objective of the Pilot Project on Marine Pollution Monitoring is to initiate and expand an internationally coordinated program for marine pollution monitoring, initially in selected ocean areas, in order to acquire and exchange among nations intercomparable data for making assessments of the periodic state and degrees of contamination of the marine environment; and, to establish the organizational machinery required for further development and expansion of marine pollution monitoring.

The objectives of the Workshop were: (a) to provide scientific and technical advice, based mainly on information supplied by the Symposium, as to the methodology (observation and reporting, sampling, sample preservation, analysis, standards criteria, data handling) to be used or initiated during the Pilot Project, and also to identify future studies needed to expand the Pilot Project; (b) to recommend technical assistance programs and training and education projects that would provide pertinent support to developing countries to enable them to establish marine pollution monitoring activities.

These Proceedings contain summaries of, plenary speeches by invited guests, summaries of papers given at the Symposium and the Report on the Workshop to support the Pilot Project on Marine Pollution (Petroleum) Monitoring.

R.C. Junghans

R. C. Junghans
Conference Coordinator

MARINE POLLUTION MONITORING (Petroleum)
SYMPOSIUM AND WORKSHOP

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Invited Speakers

R. W. Roberts
R. M. White
A. I. Simonov
B. E. Willard
P. Thacher
A. Tolkachev
E. B. Wilson
S. Hori
S. R. Galler
H. F. Casey
R. M. Morse
M. E. Stansby
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Topical Session Chairman

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II. E. M. Levy
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IV. J. W. Farrington
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V. M. Gruenfeld
VI. M. E. Stansby
Final Plenary R. L. Lehman

Rapporteurs

B. J. Thompson
A. Zsolnay
R. H. Pierce, Jr.
R. C. Clark, Jr.
T. Joyner

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Topical Session III. Standards and Intercomparison Criteria

Topical Session IV. Oil in Marine Organisms and Sediments: Sampling and Analytical Methods

Topical Session V. Tar Balls and Particulate Matter: Analytical Methods

Contributed Papers (continued)

Welcoming Address

Dr. Richard W. Roberts
Director, National Bureau of Standards
Department of Commerce, USA

Many poets have looked to the sea for inspiration. They've seen it as a mystery, as a barrier that separated people. They've pictured sea monsters and various perils. But two centuries ago Samuel Coleridge painted a very dramatic picture of a polluted ocean in the Rime of the Ancient Mariner. It strikes uncomfortably close to home these days. He said:

> "The very deep did rot...
> Yea, slimy things did crawl with legs
> Upon the slimy sea.
> About, about, in reel and rout
> The death-fires danced at night.
> The water, like a witch's oils,
> Burnt green, and blue and white.

Things aren't that bad. But the nations of the world have to view the sea as a common territory whose wealth we can share only so long as we preserve and protect it.

In March of 1968 the President of the United States endorsed the concept of an International Decade of Ocean Exploration. He stated:

> "The task of exploring the ocean's depth for its potential wealth - food, minerals, resources - is as vast as the seas themselves. No one nation can undertake that task alone. As we have learned from prior ventures in ocean exploration, cooperation is the only answer."

Two months later the International Oceanographic Commission adopted a formal recommendation supporting the Decade idea coordinated on a world-wide basis. Further endorsements came from the United Nations General Assembly.

In the first year of the Decade's existence, three areas were chosen for priority attention:

(1) Environmental quality,
(2) Environmental forecasting, and
(3) Seabed assessment.

The commitment to sharing the task of exploring and protecting the oceans brings us together this morning. Representatives from over 75 nations are here to join with the sponsors of this conference - IOC, the World Meteorological Organization, the National Oceanic and Atmospheric Administration, the Maritime Administration and the National Bureau of Standards. We have a two-fold purpose:

First we want to develop working guidelines for an international pilot project to monitor marine pollution. And we want to focus on the problems and advances in the measurement and characterization of petroleum hydrocarbons in the marine environment.

On behalf of all of NBS, I want to welcome you to the Bureau. You are visiting one of the largest physical science laboratories in the world. Our work in standards development spans a broad range of activities because, after all, standards are the currency of science. This currency is based on accurate measurement. In the area of marine pollution, we're not yet at the minting stage. Your job, beginning with this conference, is to find the best ways of measuring and monitoring hydrocarbons. The focus is very specific, and there's much to build on. But only by working together can the nations of the world build toward a solution to a global problem.

United Nations Environment Program EARTHWATCH and Marine Pollution

Dr. Robert M. White, Administrator
National Oceanic and Atmospheric Administration

Ladies and gentlemen, our government of the United States is very pleased to have the opportunity to host this Symposium on Marine Pollution Monitoring which is sponsored, as you know, by the Intergovernmental Oceanographic Commission of UNESCO and by the World Meteorological Organization. On behalf of our government I would like to express to all of our foreign colleagues a hearty welcome. You are in Washington at the right time of year and I know you will enjoy your stay here.

There is no need to emphasize to this group that marine pollution is clearly a threat both to the environmental and the economic values we all consider so important, and we are certainly dealing with a problem that is worldwide in scope and that affects both the developing and the developed nations of the world.

Marine pollution, as we all know, in our estuaries, in our coastal waters, and in the open ocean has myriad effects and, in many cases, effects which are poorly known insofar as the entire marine ecosystem is concerned. We are aware and concerned that there are significant reductions caused by such marine pollution to the capacity of our ocean waters to sustain economically important fisheries. We are aware that marine pollution reduces the recreational attractiveness of coastal waters, and so has a very serious adverse impact on economic values related to tourism. We are aware that marine pollution affects human health through contaminated fish, and, over the years, have seen many incidents in many countries of concern to all of us. These impacts of marine pollution of course are one of the reasons we are gathered here, and we are addressing a problem area that is intensifying rather than diminishing. It is a problem which is intensifying because our populations are increasing and our oceans are being used increasingly as avenues for the transport of energy resources as the world seeks to provide increased oil and gas resources by extraction from the seabed. And clearly on the horizon, is ocean mining for hard minerals on the sea floor. The problem is caused internationally and can only be solved internationally.

The ocean is fundamentally a fluid and what happens in one place in the oceans affects other places in the ocean. And so we have need for information about the state of pollution in the oceans. We want to know many things. We want to know the geographical extent of pollutants. We want to know about their concentration and the manner in which the oceans disperse or concentrate the pollutants. We want to know about the effects of pollutants on human health. And we would like to be in a position to be able to forecast the consequences of man's actions on the state of ocean pollution.

Now it is not that this problem hasn't received attention. It has received attention by many bodies over the many years, the latest of which, of course, has been that of the United Nations Environment Program. In

February, that program had an Intergovernmental Working Group meeting in Nairobi on what is now called the Global Environmental Monitoring System, an element of the EARTHWATCH program which I will be discussing later in my talk.

But the point I want to make here is that the importance of monitoring ocean pollution was recognized during the course of that conference and such monitoring was established as one of the seven major goals of the Global Environmental Monitoring System. Hopefully, the Intergovernmental Oceanographic Commission and the World Meteorological Organization, through the Integrated Global Ocean Station System (IGOSS), will be stimulated and supported by the United Nations Environment Program and will be able to translate this general concern into a working international effort.

I think it would be useful to ask where we now stand with respect to the establishment of a marine pollution monitoring system. As I have indicated, we have had many studies and analyses which identify the scope of the problems which face us, and tell us something about our present state of knowledge and where our principal efforts should be devoted. In a very general sense, I think we could say that the data we presently have on the state of ocean pollution is fragmentary at best. I think we can also say that the techniques and instrumentation for measuring pollutants of interest are principally laboratory methods and for only a few do we have methods adequate for systematic and routine data collection.

I think we must admit that we have yet to institute in any real way an international system for the monitoring of this ocean pollution. Hopefully, the Marine Pollution Monitoring Pilot Project, for which this Symposium will be a precursor, will be a first step in this direction. So this Symposium is a key element in laying the foundations for such a monitoring system.

I doubt that there is anybody in this audience who has dealt with problems of monitoring marine pollution who thinks that the task is easy. Quite the contrary. Even for very well stated problems, the costs that we face are large in that the time required for obtaining systematic results will be extensive. I think we all realize this.

I am reminded of one example in which my own organization and the National Bureau of Standards participated a few years ago. In the early 1960's, great concern was expressed by many scientists in the United States about the effects of insecticides and herbicides on photosynthesis and associated oxygen production because of possible effects on phytoplankton. We mounted a program to attempt to measure whether there indeed had been any worldwide changes in the atmospheric oxygen content. It took four years of joint effort by the National Oceanic and Atmospheric Administration and the National Bureau of Standards to measure oxygen content around the world and to demonstrate that, indeed, this effect about which people were concerned was not really there. I point this out only to indicate that here is a case of a very well-defined problem and that it was no easy task to implement even when you know what you wanted to do.

We need now to move into action, it seems to me, with a realistic plan of international participation in a program, and the program should start with the measurement of simple pollutants. To do this is currently within our capability. The program also should provide for the necessary research and development of the new techniques and instrumentation that will be required to measure other parameters. I think there is no lack of general agreement on what some of the things are that we must measure. Studies such as those included in the Studies of Critical Problems of the Environment; studies by various organizations in my country, our Academy of Science, and various government agencies; and studies by international groups such as the Special Committee on Problems of the Environment of the International Council of Scientific Unions, sub-groups of the Intergovernmental Oceanographic Commission, and the recent Intergovernmental Working Group on the Global Environmental Monitoring System. All these came to roughly similar conclusions about the nature of pollutants that we ought to be measuring in the oceans and the priorities for measuring them. These, of course, include petroleum, chlorinated hydrocarbons, and various toxic metals.

In my country there is now deep concern and there currently is action on problems dealing with the monitoring of marine pollution. There has been action by our Congress in passing laws that provide the authority to undertake such monitoring activities. Laws, such as our Marine Protection, Research, and Sanctuaries Act of 1972, for example, provide for monitoring and research on various aspects of ocean pollution. Amendments to our Water Pollution Control Act of 1972 provide for various kinds of water quality surveillance systems.

The President of the United States, in connection with our country's drive to increase the rate of extraction of oil and gas from our Continental Shelf, has directed extensive studies of a baseline nature be undertaken to give us the necessary information. We have a number of different kinds of monitoring programs now underway in the United States. There are baseline studies such as the GEOSECS Program of the National Science Foundation. There are studies, such as that being organized by my own organization, dealing with pollution effects from ocean dumping in the waters off the east coast of the United States.

I have mentioned activities now underway to establish baseline information over our Continental Shelf in connection with oil and gas developments. In the hall here, you probably saw the display of what we call our MARMAP Program, our Marine Resources Monitoring and Prediction Program, which seeks to acquire information about the distribution, not only of fish stocks, but on the various kinds of contaminants that might affect fish stocks. We also have extensive programs to examine the various kinds of microconstituents in all of the commercially important species of fish used in the United States. There is extensive technology development underway in the United States some of which you will hear about in the conference this week.

Internationally, there is similar concern and there has been action even prior to the United Nations Conference on the Human Environment at Stockholm. There were many conferences attempting to define what we ought to do about ocean pollution, but at Stockholm, as part of the conference which lead to the United Nations Environment Program, there was established the program called "EARTHWATCH," a program designed literally to place the earth and various aspects of it under a watch--and I use this term advisably--and one part of this program is the Global Environmental Monitoring System (GEMS).

The United Nations Conference at Stockholm has led to the establishment of the United Nations Environment Program and the establishment of a voluntary fund of $100 million for use over a period of five years. This fund now can be used for a variety of purposes dealing with environmental problems of concern to the nations of the World.

Now the EARTHWATCH Program involves many things besides monitoring. It involves problems of evaluation, research and information exchange. But the most immediate problem is that dealing with the monitoring of the global environment. The United Nations Environment Program Governing Council meeting in June of 1973 called for the early development and implementation of the Global Monitoring and Information Referral Systems of the EARTHWATCH Program which in turn led to the recent February (1974) meeting in Nairobi of the Intergovernmental Meeting on Monitoring. At that meeting, a number of principles were approved that would govern the inplementation of this Global Environmental Monitoring System. For example, one of the principles is that it make maximum use of existing national and international systems. This points to the importance of developing the Integrated Global Ocean Station System as one of the existing international systems. The meeting emphasized the need to move ahead--now--with the monitoring of critical environmental conditions for which we have the scientific and technological capability. It recognized the need to assist developing nations to enable them to participate in this worldwide activity of concern to all. I indicated earlier that one of the seven goals of this Global Environmental Monitoring System, now internationally agreed upon, was indeed the study of man's impact on the ocean. Among the other goals, of course, were questions of human health, natural disasters, food contamination, man's impact on the climate, and the stability of ecosystems. The major point here is that we now have worldwide agreement within the United Nations Environment Program to move ahead with one of its major goals, a program to study man's impact upon the ocean--and that means ocean pollution.

At this meeting there was also agreement on a priority list of pollutants to be studied. While there were some surprises in the priority ordering of this list of pollutants, I don't think the list will take any of you by surprise. It merely emphasizes that petroleum and petroleum products remain among the critical elements that we need to monitor in the oceans.

It is my hope that as a result of these decisions taken within the United Nations Environment Program and as a result of the fact that there is now a funding mechanism through the voluntary fund of the United Nations Environment Program, that it will be possible to move ahead with this Integrated Global Ocean Station System (IGOSS) which is sponsored by the Intergovernmental Oceanographic Commission and the World Meteorological Organization. Already, we can begin to see some of the results of some of the funding of that program. The United Nations Environment Program has already provided support for the GESAMP (Group of Experts on Scientific Aspects of Marine Pollution). They have provided support for the travel of a number of the delegates to this Symposium, and they have provided support for certain intercalibration efforts between the Intergovernmental Oceanographic Commission and the International Atomic Energy Agency. And, if we can come up with appropriate plans to demonstrate what it is that we can and want to do in the way of international monitoring of ocean pollution, I hope that we can convince them that this would be an area for worthy expenditure of the funds of the United Nations Environment Program.

So I think the timing is right for this Symposium. There are resources available to move ahead with a program, and there are plans for the Pilot Project. I think we have the right vehicle to do the job in this joint program of the IOC and WMO, and I know that with Symposia such as this and the results that will emanate from them, we can move ahead.

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* Scientific Problems of the Systems for Global Monitoring and Investigation of Oil Pollution in the World Ocean

Professor A. I. Simonov
Oceanographic Institute
U.S.S.R.

Mr. Chairman, ladies, and gentlemen. First, let me thank you for the opportunity to address this esteemed gathering on a very important and serious subject. Please accept my apologies for using more than my allotted time; this is necessary because simultaneously translation of my report, as I read it in Russian, is a slow process.

Mr. Chairman. At first I planned only to comment on the text of a draft program of global observations and explorations presented by me last year to the Intergovernmental Oceanographic Commission, (First Session of the International Coordination Group for Global Investigations of Pollution in the Marine Environment). This numbered report was distributed to Members of the Commission in both English and Russian language versions. Later, I decided that because two years had passed since the program was initiated, a more complete discussion was warranted.

In my report I will describe or comment on the following items. First, the background of the problem; second, the global character of the problem under consideration by this gathering; third, the role of hydrodynamic factors in the movement, dispersion, and accumulation of harmful pollutants; fourth, the kinetics of dispersion and disintegration of the various forms of oil and oil products in the marine environment and the disintegration forms of these oils; and, fifth and last, I will discuss the main elements of the scientific basis for a global system for monitoring and investigating oil pollution in the world's oceans. Thus I have divided my report into five sections.

In considering the background of the problem, we must first consider the nature of the problem. As I see it, the nature of the scientific aspects of protecting the marine environment from pollution can best be determined by working out scientifically based recommendations for regulating or completely prohibiting the discharge of wastes containing petroleum hydrocarbons. Accordingly, processes utilizing harmful substances should constantly be monitored so that waste disposal methods can be developed leading to the complete elimination of pollution effects in the water medium and on ecological systems. This recommendation covers a wide range of problems. Among the most important actions needed to deal with the problem are the following:

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* This is an English translation made from the speech given in Russian and recorded on tape. Due to technical difficulties beyond our control, clearance by the author has not been obtained.

(1) A continuous and systematic monitoring and evaluation of oil and oil product pollution conditions in the waters of the world oceans.

(2) Studies of the increasing utilization of oil and oil products as these uses affect the seas.

(3) The development of regulations concerning the discharge of substances containing petroleum originated hydrocarbons into the sea.

The difficulties of dealing with these problems lies in their complexity and their interdisciplinary nature. The level of current knowledge in the various oceanographic disciplines, such as the chemistry and the kinetics of the seas, requires a considerable amount of development to enable their use in the solution of these problems. And the last, but not the least of the factors that must be considered, is the ubiquitous nature of the world's oceans. The seas, like the atmosphere, know no national boundaries; pollution originated by one nation is not the problem of just that nation but of all the nations of the world. The international convention that met in London in 1972 agreed that oil and oil products should be considered the most widespread pollution substances affecting the world's oceans. Various sources estimate that ten to fifteen million tons of oil substances are dumped into the oceans annually. No doubt this pollution will increase at an ever growing rate as oil production increases and as the major part of the production is moved from land to the continental shelf and farther out to sea. I would like to remind you of the catastrophic effects of oil and oil products on the biotic regime of the oceans. Oil has extremely harmful effects on a number of links in the biological chain, links that were created over untold millenia. Together with this, oil films on the oceans have a considerable effect on the exchange of heat, gases, and water vapor between the sea and the atmosphere. It is not too far fetched to predict that extensive and persistent oil films on the surface of the seas could have serious effects on the climate of the earth and the oxygen content of the atmosphere.

Now to my second point; the global character of the oil pollution problem and the proof that the problem is truly global. Until recently, we had no data with which to characterize the degree or extent of pollution of the waters of the world by oil and oil products. Many of you here will remember an address by Tor Hyerdahl at the London conference during our preparations for the Stockholm conference. Hyerdahl reported on his visual observations and impressions on the extent of oil pollution in the North Atlantic. At that time, his was perhaps the only direct source of information on such pollution. This report inspired experts from a number of countries, including the USSR, to make a series of observations of pollution conditions in the North Atlantic and the seas that wash the coastal areas of the European continent during the period 1971-73. The primary reason for these observations was that, at that time, both the semi-enclosed Baltic Sea and the completely open Barents Sea were heavily polluted by oil and oil products. A number of very important conclusions about the character of oil pollution in certain parts of the oceans were made possible by analyses of these observations. The most important conclusion drawn was that oil pollution in the oceans is now global. Today, it is equally probable that petroleum hydrocarbon pollution exists and can be observed in any part of the world's oceans, including the continental seas, the coastal waters, and even in the open oceans. Another important conclusion is that fields of oil pollution, which originate primarily near the shores, spread out to cover entire inland seas and even certain large areas of the open oceans. The seas that wash the edge of the European continent are polluted with oil and oil products; the amounts of pollution exceed the Soviet Union's maximum allowable concentration of 500 parts per million. The Baltic, the North Sea, the Irish Sea, the Bay of Biscay, and the Tyrrhenian and Ionic Seas are entirly covered by oil pollution. While the concentration of pollutants in these relatively enclosed seas decreases with distance from the shore, the concentrations at distances hundreds of kilometers from shore are still greater than the USSR allowable maximum. The same conditions obtain in other parts of the open oceans. The highest concentrations of pollution substances have been measured in near-shore areas and in the vast, relatively quiet areas of the open ocean to which they are carried by the Gulf Stream and the North Atlantic current. (I will deal with this problem in detail in my paper tomorrow.) Thus, at present, we have a basis to believe that oil pollution is quite global in character. I would like to note that these conclusions contradict to some extent those stated by Menaham and others in their report entitled "The Content of Stable Hydrocarbons in the Sea Along the Line of Tanker Ships." Their conclusion is that oil basically spreads in a thin layer up to ten meters in depth. It seems to us that this conclusion is not completely substantiated because the water samples were taken only in the layer from the surface to a depth of ten meters. Further on, I will show that oil pollution can be found deeper -- much deeper -- and that its spread depends on the vertical circulation, the position of the thermocline, the form of the oil products, and the time they have been in the water.

And now the third section of my report. Here I will discuss the influence of hydrodynamic factors on the spreading, dispersion, and accumulation of oil pollutnats. Analyses of the horizontal spread of petroleum pollutants shows that minimum concentrations occur in the fast moving water in the middle of ocean currents and maximum concentrations in the peripheral regions of turbulence. The vertical distribution of oil products is multi-layered in the extreme. The greatest numbers of layers containing concentrations of oil were found between the surface and ten meters down and again between fifty and one hundred meters down. Sometimes these concentrations were registered at even greater depths. The nonuniformity of the spreading of oil products is attributable to their variation in form, the length of time they have been in the water, and the peculiarities of the circulation and vertical structure of the water. In sea waters, oil products can take many forms: emulsions, floating films, lumps, and even solutions in small amounts. Thus, oil products, which are basically in the form of dispersed particles that increase in weight with time, will, under normal conditions, be carried from dynamically active zones under the influence of the Coriolis acceleration and transverse currents to relatively calm zones where they will accumulate gradually. Bearing this in mind, we can expect that accumulations of oil pollutants will gather both on the surface and to some depth on the outer periphery of cyclonic whirls and in the inner zone of anticyclonic whirls. This is completely confirmed by measurements taken in the North Atlantic (which I will report on in my paper tomorrow).

The fourth section of my report deals with several of the most important chemical and physical aspects of the nature of pollution in the sea. I will be brief because these problems will be dealt with in detail later in our Symposium. Experimental investigations on how the concentration of oil changes with time show that the first reaction that takes place is saturation of the sea water by oil. This process can last for as long as ten days. After saturation has occurred and a state of equilibrium has been reached, the interaction between microchlorine and oil initiates a process of intensive disintegration of oil products, which can last for ten, fifteen, or as long as twenty days. After that, the speed of disintegration slows up considerably. This experiment reveals the characteristics and the general features of the disintegration of oil products under the influence of chemical and microbiological factors. Experiments on natural models have shown that physical and chemical oxidation play very important roles in the disintegration of oil products; this is a type of free-radical process. About sixty percent of the oil is decomposed by chemical and physical processes which act in a fashion similar to the process that causes monomolecular reactions. Together with these experiments, we initiated steps to investigate differentially the processes involved in the disintegration of oil components. The results of these investigations show that, first, normal algae disintegrate very rapidly and then the aromatic hydrocarbons begin to disintegrate. This process takes place at a slower rate because disintegration of the aromatic hydrocarbons requires larger amounts of oxygen. Our results are confirmed by the conclusions reached by a number of American experts who have shown that all petroleum hydrocarbons can be oxidized by bacteria. Hydrocarbons with long chain structures can be destroyed faster than those with short chain structures. Many aromatic hydrocarbons are less subject to oxidation than are petroleum hydrocarbons with direct or branched chains. It is our impression that the aromatization of molecules makes their micro-oxidation difficult, perhaps because of their inherent stability. For a number of the aromatic hydrocarbons investigated, a characteristic feature is that oxidation takes place because of the presence of short-chain proteins. In parallel with this investigation, we investigated the role of micro-organisms in the oxidation of oil products. It has been stated that the period of quickest reaction in the disintegration process is speeded up by the initiation of oil oxidation processes and by the actions of all of the heterotropic micro-organisms. In recent papers, the problems of the chemical nature and the physical and chemical characteristics of the oil oxidizing process are considered according to the hydroperoxide theory of branched chain oxidation, the details of which were worked out for hydrocarbons in the liquid phase by Emmanual(?). It was stated that hydroperoxide, which is the initial product of oxidation, is responsible for the degenerative branching out of complex chain oxidation. On the basis of this information, scientists of the Soviet Union have elaborated methods for controlling free-radical processes in the physical and chemical utilization of products such as petroleum hydrocarbons. In concluding this section of my report, I would like to mention that the period of semi-disintegration of oil under similar conditions may be as long as fifty to seventy days, and that the later period -- when the disintegration is slow -- is prolonged and of indefinite duration. So the experts, including scientists from the countries sponsoring this Symposium, are absolutely correct in asserting that petroleum-originated hydrocarbons decompose in the same way that other natural hydrocarbons have decomposed during geological epochs in the past. Because of these principles, concentrations of oil can and do occur in the oceans and in the sediment, particularly under low temperature conditions.

And now for the fifth and final section of my report in which I will speak of the main scientific principles for a global system of investigating and monitoring oil pollution in the world ocean. I would like to remind you that the observations mentioned above make it possible to define the characteristics of this system. The principles we are concerned with are the following: first, the system of observations should take into account the latitude and the zonal changes in thermal conditions so we can study the influence of different temperatures on oil degradation. Thus, this system should extend from the Equatorial zone to the Arctic zone of the North Atlantic. Second, the observational system should be designed to take into account the varied hydrodynamic conditions of the ocean. Some stations of the network should be positioned in the main circulation currents so, on the basis of observed motions, we can make quantitative predictions on the transport of oil and oil product pollutants. Other observation points in the system should be located in relatively calm zones of the ocean so we can keep a continuous record of the accumulation of petroleum pollutants. For example, in the North Atlantic, part of the network should cover the Gulf Stream and the North Atlantic Current, as well as other parts of the system, the northeastern sector of the Sargasso Sea and the Barents Sea. The third consideration is toward monitoring the basic sources of oil based pollution. These sources are the shorelines, the continental shelf, and the navigable shipping routes along and connecting the continents. One does not have to prove that the North Atlantic is the most polluted ocean region of the world; the existence of large numbers of pollution sources in the area tells us intuitively that this is so. The principles just mentioned lead us to the formulation of the fourth principle, which is that the system of observation must be usable for solving the balance equation for oil pollution in this or any other area of the world ocean. The balance equation mentioned is the one I wrote for the IOC program, the Global Investigation of Pollution in the Marine Environment (GIPME). For the left part of the equation, I calculated the increase of the concentration during a certain period of time, (e.g., a year), and for the right part of the equation all of the remaining components of input and consumption of oil products in sea water. The solution for the balance, in turn, requires that the observation system be so located that it will account for the advection of oil, its redistribution in the vertical, its sedimentation into soils, and its evaporation from the sea surface. The observation system should provide not only for the taking of samples from the surface and from below the surface, but also for measuring the specific horizontal and vertical dimensions of sea surface oil films — bearing in mind that the presence of these films can influence considerably the important interactions between the atmosphere and the ocean. This requires observation not only by surface vessels but also the location and observation of these films by orbiting satellites.

These four principles require the organization of a complex system to obtain meteorological, hydrochemical, hydrological, and hydrobiological observations of the seas, the marine population, the bottom sediments, and the air-sea boundary layer. These systematic observations should be carried out in "benchmark" or "signature" regions. Regions not subjected to pollution and for which standard smaples should be obtained, I call number one regions. The number one benchmark regions should be investigated during the process of reconnaissance over all oceans and at different geographical latitudes. Simultaneously, systematic observations of number two, or polluted benchmark regions, should also be carried out. Number two benchmark regions include the most polluted areas of the world ocean, those areas near the months of large rivers, large industrial and residential areas, areas of underwater mining of minerals, petroleum, sand and gravel, and other areas of possible sources of induced pollution. These special observations should be made periodically, say two to four times a year, using both region one and region two benchmark stations as anchor points in the observational network. Before activating a global observation system, it also will be necessary to determine by reconnaissance the degree and specific distribution of oil pollution in the open waters of the world ocean. These benchmark observations must be available for planning the systematic observation and monitoring of oil pollution. It apparently will be necessary to start with an experimental demonstration project before setting up a global system. In my opinion, the Atlantic Ocean would be the most suitable demonstration area. For any observation network, it is necessary that we unify and standardize the methods of chemical analysis, the measurement of physical characteristics, and the means and methods of selection and storage of samples. These are problems for consideration at this Symposium.

This, in brief, is my report. I am sure that our Symposium will result in a definite plan for an experimental demonstration project for observing and monitoring oil pollution in the world ocean. Thank you for your attention.

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Environmental Quality

Dr. Beatrice E. Willard
The President's Council on Environmental Quality

Thank you very much Mr. Junghans. It is a particular privilege for me to address such an illustrious group on a very, very important topic to all of us. This topic, as we are all aware, relates both directly and indirectly to human survival on Planet Earth. During the past year, we at the Council on Environmental Quality have focussed sharply on this topic. Just over a year ago, the President asked us to prepare for him a report on the environmental effects of oil and gas development on the Outer Continental Shelf of the Atlantic Coast and the Gulf of Alaska, two areas that have never had any oil and gas development. That report, delivered to the President on the 18th of April, 1974, gave us an opportunity to summarize what is now known about the environmental aspects of those areas and about the technological and methodological aspects of controlling the acute and the chronic effects of marine pollution from the variety of activities associated with off-shore oil and gas development, not just from transporting oil.

It was sobering to all of us to see how little really was known about the direct biological effects of oil and gas pollution in the marine environment. It was even more sobering to me, as a professional ecologist, to realize that we were still not truly recognizing the real nature of the environmental problems in this particular area. That is a rather strong allegation and I would like to explain what I mean.

In the time that I have been serving on CEQ, I have noticed that policy-makers often have a human tendency--which all of us have, but which scientists try to overcome, to conclude that because there are no dramatic, clear-cut, immediate effects visible from oil spills, beyond a few birds drowned and a few feet of shoreline covered with oil for a few years, that there likely are none. This conclusion is not surprising because it represents generally the way in which people think; it is an example of the results of how without scientific expertise, people go about gaining knowledge.

We have had a sophisticated scientific potential for obtaining ecological and physiological knowledge for over a century. Some potential we have had for two or three or four centuries, because man is very curious. He has been finding out what species are there and what their habits are for centuries. But, because the marine environment presents him with more of a challenge than the terrestrial environment, man has not been able to find out as much as is needed to understand the life requirements of marine animals, and what the introduction of oil and gas into their environment means to them.

We now have the scientific techniques, considerable knowledge and the potential to test the effects of oil and gas on all marine organisms. Some will present more of a challenge than others. We have the ability to monitor even subtle changes in both shoreline and pelagic marine ecosystems. Then why is little being done compared to what needs to be done? It is because "it is too expensive." Too expensive in whose terms? In the biologists' terms? In the ecologists' terms? In Wall Street terms? In Government terms? In petroleum companies' terms? And are we, when we are working out the expense, determining, in addition to the dollar value, all it will cost to find out this information? And what it will cost us, if we do not find it out in time to protect those populations on which we depend for food? Are we really looking at costs from the human survival terms, as well as biological terms, where time and evolutionary response play a big role in the equation?

I think all of you will agree that we are only beginning to understand the vast ecosystems of the ocean. We must be sure that we are not selling their needs short by a superficial short-range view of effects that we often cannot determine fully within the short range of our rather inadequate attempts to really understand the systems and the effects of oil on the systems.

Because we are at this point in time, because you are a very diverse group, and because the demands of scientific discipline force us constantly to become more and more specific, I want, this morning, to be more general. This will enable us to focus on what I find a most helpful group of guideposts for better policymaking, ecological research, and environmental control.

This is a group of seven choices. All of us here will realize that the choice intelligently can only be made in one direction. This is a choice between doing what is most economically expedient at the moment and recognizing, utilizing, and living by a group of scientific principles of ecosystem operation. I think all of you would agree that we have to choose obeying principles of ecosystems, even though it may take a certain amount of rearrangement of our own viewpoint, rearrangement of what we are willing to accept as true, as a result of what we believe our own five senses are telling us.

To me, the most important principle is that everything affects everything else, either directly or indirectly. This is a valuable guiding principle, not only for ecology, but for all activities of humankind. The environment, ecosystems, social systems, etc. are wholistic, integrally connected, and interdependent.

This one principle leads me to a very conservative viewpoint on how we should treat the oceans of the world. But it is not easy for non-biological, non-scientific people to accept, because they have a very difficult time believing that the actions that they take today will have ramifications a hundred years, a thousand years, and even ten thousand years from now, because they cannot see that far into the future. Unfortunately, we do not have the scientific background to give them that vision. You and I have to provide that for them. I want to compliment Dr. White for having this Symposium, where we can get together to really plan how to research the knowledge for them to use.

The second guiding principle of ecosystems is a self-evident choice to those of us who are familiar with the natural world. Yet it comes as a revelation to those not trained in the scientific disciplines. This principle is that the whole biosphere of Earth is divided into systems. We, as ecologists, call them ecosystems. In them, all living things have specific roles to play. This is difficult for us to accept when we believe that some of those roles are not useful to man. Some of the roles are even detrimental to man. We could all do without mosquitos if we had our emotional choice. A friend of mine points out that if he had been given the job fifty years ago to do away with the fifty most obnoxious plants, he undoubtedly would have done away with that awful bread mold, penicillin. That action would have deprived man of a valuable medicine. I think that intellectually all of us realize that all of the natural phenomena eventually are going to be shown to be directly and indirectly very important to us. But this fact is sometimes hard to sell today.

The third principle is that all materials cycle, but energy does not. This principle is one which we have had to come to grips with in the last eight months, one which has made us realize we have to find new conservative ways of using energy and new ways of finding out where the toxic substances which we put into the system go. We are not anywhere close to this understanding, as you know better than I.

Another principle that is hard to convince man of is that all living systems and non-living systems have limiting factors. Engineers are quite ready to accept that we can put only a certain amount of weight on top of a building before something happens; that if we exceed that weight, we would ultimately have disastrous results. But they do not quite see that a natural system also has these constraints. They feel, "We can handle that technologically, we're always going to discover a technological fix for the problem." This may be true, but if they were going to handle problems technologically for a building, they would design for possible limits before they tried to put the weight on the roof; they would not design after the fact. I think that all we expect in ecosystem management is that we not put stresses on these systems beyond what we know they are capable of absorbing. Yet all the time we push in all directions--"cut more trees," "harvest more fish," "put more oil into the water"--because we haven't seen the effects yet. But we have not lived long enough for a lot of those effects to occur.

The fifth principle--closely related: all systems have a carrying capacity. This principle interacts closely with the fourth, but these concepts do not come naturally to the non-biological, non-technical, non-scientific thinker. He thinks automatically that "There is going to be a technological fix. Because there will be a technological fix, the carrying capacity of any human system cannot be determined. Therefore, there is no point in trying." This is just like walking off the cliff without a belay rope.

The sixth principle is equally important, i.e., all ecosystems have a series of developmental phases through which they pass in their life histories. These phases range from the simple, very unstable ones to the complex, stable phases. We tend to believe that only the simple phases are productive for us.

The seventh and last principle is that as specialization occurs, more diveristy comes into the system. With more diversity, they have greater and greater stability. Constantly man is selecting against diversity. He thinks he doesn't need California condors, and that grizzly bears aren't all that important--without the knowledge of how these animals affect the total system. It is as though we were electing not to recognize the value of molybdenum in stress steel, when in fact the molybdenum is the very thing that makes the steel able to stand the stress.

As we candidly approach the marine systems--as you will in the next two and a half days--seeking to understand their functioning and the needs for that functioning, I am sure you will be able to determine more about basic ecological costs and benefits, as well as the economic costs and benefits of these systems to man. I am very impressed with a piece of work a famous ecologist recently has done in Georgia. Dr. Eugene Odum of the University of Georgia has found that saltgrass marsh along the Georgia coast, if filled so that it can support a shopping center or housing or an industry, would sell at between $1,000 and $3,000 an acre. This value would happen once, because it would likely be a terminal sale of land. But he has calculated that each year the various jobs that those saltgrass marshes are doing for us: as nursery beds for many of our different fishes, as the source of nutrient for the pelagic forms further out at sea, as cleaners of air and water pollution, as buffers for the hurricanes, and many other contributions that he has unearthed about this particular system, are worth an annual $85,000 per acre.

I am challenging you people in this room to see if you can arrive at similar calculations to help us to convince people of the subtle but real values of maintaining healthy ecosystems on Earth. When we have honestly done this, choosing to recognize, accept, and use the basic principles of ecology as governing--which they are--and not the man-made objectives that run counter to ecological principles, we will begin to experience greater environmental quality on Earth. We will begin to do what the National Environmental Policy Act of out Nation demands of us, i.e., to "bring man into harmony with his environment."

The ecologists would say it a little differently. They would say we will begin to learn how to assist man in assuming his ecological niche on Earth. I trust that we soon will accept this challenge, and solve the problems that lead to this objective. I look forward to what you can contribute in this direction in the next few days.

Dr. Peter Thatcher
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On behalf of UNEP's Executive Director, Maurice Strong, I would like to express the hope that the results of your work here will contribute to the goals governments have established for the UN Environment Program. We will judge our ability to use the resources available to us to support the work programs that are developed in groups such as this on the basis of the obvious criterion, the degree to which they contribute to the objective of our programs.

What is the overall objective? Simply put, to preserve and enhance the quality of the environment for present and future generations. It is clear that knowledge alone is not sufficient to accomplish the objective. Unless knowledge is presented in a form which is compelling to the decision-maker at the national or international level, his decisions will continue to reflect the fact that the data that comes out of the economic world, and the immediate political world, is a good deal harder and more reliable than the data that reaches him from the scientific world.

We have an opportunity to change this situation with regard to the oceans, one which has been growing over the years, one which, if we fail to exploit now in the next few years, may not arise again. The opportunity is based on the political willingness that governments have registered to do something about that part of this planet which lies outside the limits of national sovereignty. At the Stockholm Conference we found a high level of willingness by governments to commit themselves in general terms to the actions that must be taken if man's effects on the oceans are to be reduced. So I think that the burden comes right down on you to develop, with precision, not only the parameters to be measured but the techniques involving intercalibration, particularly, on which rest the softness of so much of the data presently available to the decision maker. We must acknowledge that we are using the oceans, we are using man's common concern to protect the oceans, as one of the many devices by which to attack the problem at the source. For example, most of the petroleum reaching the oceans, still of course, comes from land. We have seen considerable progress with regard to maritime sources. There are new laws and new conventions, which have the capacity of binding states to adhere to new principles of design with regard to vessels. There is the recent achievement in London of an Ocean Dumping Convention, which attacks the broad problem of deliberate waste, where nations have traditionally followed the natural geological process of using the oceans as the garbage pail for waste they do not want to dispose of on land. In recent weeks, the government of France has achieved, I think, a very significant breakthrough in the form of an international agreement on the part of a number of European states to coordinate their attack on marine pollutants which reach the oceans thru river input and direct outflow. I think that the significance of this is that here is a collective effort, for the first time, to go up the rivers, to go into the municipal sewer system, to find out where the critical valves are that must be turned off if any significant difference is to be made. The area that is politically and scientifically still far in the future is the area of atmospheric transfer, which in the case of petroleum remains an important route by which petroleum hydrocarbons reach the oceans of the world.

What we need is hard data gathered with intercalibration in a system whose design in time and space and quality controls are adequate to demand the attention of decision makers. Otherwise they will continue to shy away from decisions which would have a beneficial effect on the oceans. They will continue to be preoccupied by the fact that a good piece of marsh is only worth a thousand dollars.

So I think that the challenge is clear.

UNEP's role in this, at the international level, is to use the resources that we have been given to catalyze new efforts and attract new resources. The Environment Fund, hundred million, sounds like a lot. But those of you who know the scope of the program that confronts the world community realize how terribly insignificant even this much money is relative to what needs to be done. And this means of course, that the real work has to be done at the national level. The role of the international agencies, particularly those who have sponsored this meeting, is to help governments work together more efficiently. The applicable lessons came out of the IGY and the exploration of Antarctica, and they are practiced today in programs such as the World Weather Watch, which have immediate practical, tangible results for rich and poor around the world. The real work, of course, has to be done by you. We are very happy that you're doing it. We hope that your results will come to us in the form of specific proposals. The expected results must be clearly defined and the use of the data well understood. We will then see how, for our part, we can make the international system work a little bit faster, more energetically than it might without our help. Thank you very much.

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Pilot Project on Marine Pollution Monitoring under the Framework of IGOSS

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Intergovernmental Oceanographic Commission, UNESCO

First of all, allow me on behalf of the Secretary of the Intergovernmental Oceanographic Commission (IOC) to express our deep appreciation to the Government of the United States for hosting this Workshop and Symposium, for the preparatory work that has been done and the excellent arrangements that have been made. We wish to express our thanks and appreciation to the United States Agencies that have been involved in the organization of the Workshop and Symposium: the National Bureau of Standards, the National Oceanic and Atmospheric Administration, and the Maritime Administration of the United States Department of Commerce.

For several years the problem of marine pollution has been one of the major problems under consideration and study by the IOC. A number of resolutions have been approved by IOC emphasizing the need to undertake specific studies of various aspects in the field of marine pollution and recommending specific action to achieve these goals. The marine pollution problem has been outlined as one of the key problems in IOC's basic program of work--the Long-term and Expanded Programme of Oceanic Exploration and Research (LEPOR), approved by the IOC in 1969. The central role of IOC in promoting and coordinating scientific programs and services in the field of marine pollution was recognized by the United Nations Conference on the Human Environment, Stockholm, June 1972.

At present, various aspects of this problem are under consideration, and studies are being made by groups established by IOC or set up by other international bodies to advise the Commission. In particular:

- the Group of Experts on the Scientific Aspects of Marine Pollution (GESAMP) is a joint, specialized group consisting of experts nominated by the Inter-governmental Maritime Consultative Organization (IMCO), the Food and Agriculture Organization of the United Nations (FAO), the United Nations Educational, Scientific and Cultural Organization (UNESCO), the WMO, the World Health Organization (WHO), the International Atomic Energy Agency (IAEA) and the United Nations--which was established to provide advice to the sponsoring organizations and to IOC on desirable action to be followed in this field, taking into account the latest state-of-the-art in matters relating to the scientific aspects of marine pollution;

- the International Coordination Group (ICG) for the Global Investigation of Pollution in the Marine Environment (GIPME) is responsible for preparation of a comprehensive plan for implementation of GIPME, including specific recommendations for long-term coordination of the program and the establishment of priorities for the projects contained in the Plan;

- the IOC Working Committee for IGOSS, jointly with the WMO Executive Committee Panel on Meteorological Aspects of Ocean Affairs (MAOA), and the subsidiary bodies of the Working Committee--particularly the Group of Experts on Oceanographic Research as it relates to IGOSS (IRES)--are dealing with design, planning and development of the marine pollution monitoring program;

- the IOC Working Committee on International Oceanographic Data Exchange (IODE), and particularly its ad hoc group on marine pollution data, is responsible for development of procedures for exchange, storage, archiving and retrieval of marine pollution data and information; and

- the Scientific Committee on Oceanographic Research (SCOR), together with other scientific advisory bodies to the Commission and the International Council for the Exploration of the Sea (ICES), has established a Liaison Panel on marine research related to pollution to correlate the activities of the subsidiary groups of the sponsoring organizations.

It is obvious that all these studies and investigations are based on national activities, and success in this field on an international level depends on the efforts undertaken by countries, national agencies, national research institutions, universities, and individual scientists. Several countries have already initiated such investigations in certain marine areas on a national level or on an international level, especially in such areas as the North Sea, the Baltic Sea, and the Mediterranean Sea.

It was recognized that, in order to review the state of the ocean and its marine resources as regards pollution and the forecasting of long-term trends, a worldwide system of monitoring of the constituents of marine pollution should be established. The need for the establishment of such a monitoring system was emphasized by the seventh session of the IOC and the 24th Session of the WMO Executive Committee; these governing bodies of IOC and WMO decided that the Integrated Global Ocean Station System (IGOSS) provides a suitable framework for the coordination of marine pollution monitoring activities in respect to physical and some chemical parameters. Furthermore, the United Nations Conference on the Human Environment, Stockholm, June 1972, also recommended that the IOC, jointly with WMO and, as appropriate, in cooperation with other interested intergovernmental bodies, provide the monitoring of marine pollution, preferably within the framework of IGOSS.

In light of the above decisions and recommendations, IGOSS planning and subsidiary bodies recommended, as a first step in this direction, that a Pilot Project on Marine Pollution Monitoring be developed and that it should focus on oil and dissolved petroleum constituents; they then prepared an Operational Plan for such a Pilot Project. Some of the experts sitting here took an active part in its preparation: Dr. Ehrhardt (FRG); Dr. Levy (Canada); Dr. Simonov (USSR); Dr. Zafiriou (USA); Dr. Zsolnay (Bermuda); R. Junghans (USA); T. H. Thompson (Sweden); and others. This Plan is now before you as document IOC/WMO-IPLAN-II/3. It was endorsed by the IOC Assembly at its eighth session in November 1973 (Resolution VIII-20).

The basic purpose of the Pilot Project described in the Operational Plan is to initiate the operational phase of a marine pollution monitoring program on an international level, and on a large-scale basis, and to establish the necessary organizational machinery to enable it to discharge its coordinating role in a developing marine pollution monitoring program.

The selected vehicle for this project is petroleum derived oils since it is possible to base a Pilot Project capable of involving nations with widely varying degrees of expertise and capable of providing examples of the type of organizational problems which will have to be overcome in any coordinated exercise on marine pollution monitoring.

The Pilot Project will have to determine the state of oil pollution in certain oceanic areas and to specify the areas and frequency of observations for a future oil monitoring system. Its further development will enable us to evaluate the variability of pollution by oil in time and space for operative purposes, and seasonal and year-to-year trends.

Internationally coordinated procedures will have to be developed during the Pilot Project on sampling and on the preservation and analysis of water samples, on formats for data reporting and exchange, and on the content of products and services to be provided on an international level.

From the Operational Plan it can be seen that the Pilot Project will be restricted initially to areas of the North Atlantic and adjacent seas and waters around the African continent; these have been selected taking into account the regions of offshore oil production, the main routes of oil transportation, and ocean current patterns.

For the Pilot Project, it is recommended that the following be monitored: oil slicks and other floating pollutants; particulate residues or "tar balls"; and dissolved petroleum hydrocarbons in the surface water and in the water column. Procedures for observations, sampling, and reporting of the above parameters, as recommended for the Pilot Project are described in the appendices to the Operational Plan. To evaluate the results of observations and measurements, simultaneous observations of sea temperature, salinity, dissolved oxygen, air temperature, wind, currents and waves are also recommended.

In preparing this Operational Plan, it was understood that initially all the above measurements and observations would come from research vessels, ocean weather ships, and suitable offshore platforms, especially with regard to dissolved petroleum hydrocarbons. However, it is clear that, even at this stage, other vessels suitably staffed and equipped should be involved in the Project.

Recognizing that parts of this program are already underway, it is nevertheless proposed that the Pilot Project begin on 1 June 1974 and run for a 24-month period during which activities would be expected to intensify. Periodic evaluation of the results of the Pilot Project will be undertaken with the assistance of a Task Team consisting of individuals to be designated by national coordinators for the Pilot Project, who will also be responsible for preparation of a comprehensive report, to contain details of management and scientific aspects. This report will be evaluated in conjunction with the ICG for GIPME and recommendations will have to be made to the IOC Working Committee for IGOSS and the WMO Executive Committee Panel on MAOA for the next steps to be taken in marine pollution monitoring.

A global monitoring system has to be developed through progressive integration of existing national and regional systems, and monitoring programs into an internationally coordinated program, and by encouraging their development in other countries on the basis of the experience. Therefore the IOC and WMO Secretariats, in accordance with recommendations of the eighth session of the IOC Assembly and the second session of IPLAN, requested Member States of both bodies, by Joint Circular Letter No. 10, to provide details of their interests and how they can contribute to the development and implementation of the Pilot Project, and also to designate national coordinators. Up to now, replies have been received from 26 countries, 16 of which expressed their interest and willingness to participate in the Pilot Project namely: Argentina, Canada, Egypt, the Federal Republic of Germany, Iceland, Indonesia, Ireland, Japan, Korea, the Netherlands, Nigeria, Poland, Thailand, the United Kingdom, the USA, the USSR, and Uruguay. Several other countries have designated national coordinators and will shortly provide details of their participation--Australia, Belgium, France, Greece, and Norway. Details of national replies are presented to you as document IOC-WMO/MPMSW-I, the report of Task Team I for the Pilot Project.

The Joint IOC/WMO Planning Group for IGOSS recommended that a Workshop and Symposium should be convened to develop further the necessary working guidelines for the Pilot Project on Marine Pollution Monitoring, according to the Plan developed in August 1973. This is one of the basic objectives of this Symposium and Workshop, as outlined in the final program.

The Joint IOC/WMO Planning Group for IGOSS expected that the Workshop would review the Operational Plan for the Pilot Project and provide recommended procedures and methodology for use by national coordinators in the implementation at the national level of the operational programs for the Pilot Project. Immediately thereafter, a meeting of the Task Team will be convened here, with participation of some experts presently at this Symposium and Workshop, to apply the results of the discussion to the Operational Plan and to finalize it for presentation to participating Member States.

To facilitate their work, several items and questions have been addressed by the Joint Planning Group for IGOSS to the Workshop for consideration. Allow me to point out the basic ones:

- procedures to be recommended for observing, sampling (including preservation and analysis of samples), and reporting of oil slicks and other floating pollutants, particulate petroleum residues (tar balls), and dissolved petroleum hydrocarbons;

- recommendations as to preparation of relevant manuals, guides, and instructions on operational and technical procedures for use by participants;

- identification of further studies required for intercomparison and intercalibration of sampling and analytical techniques and methodology, including standards and intercomparison criteria; and

- recommendations as to new methods for monitoring of oil and dissolved petroleum constituents, including the use of satellites, biological indicators, and other parameters.

Here I wish to point out that the Group of Experts on Oceanographic Research as it relates to IGOSS, at its fourth session (April 1974), stressed the importance of such observations from voluntary observing ships and requested the Symposium and Workshop to consider the development of instruments and methods simple and reliable enough for use on non-specialized ships without interfering with their normal operation, as well as development of automated equipment for future use aboard those ships so that demands on the ship's crew will be kept to a minimum.

With reference to the specification of recommended locations for monitoring and possible other ocean areas to be included in the Pilot Project, the fourth session of IRES wished to draw your attention to the work undertaken by Japan, described in the document entitled "Tar ball distribution in the Pacific and Indian Oceans". IRES-IV requested the IOC Working Committee for IGOSS to consider inclusion of the ocean areas around Japan in the Pilot Project.

The IOC Working Committee for IODE has been requested to consider standardization of methods and forms for reporting, dissemination, exchanging, and archiving of information arising from the marine pollution monitoring program. However, your views on this topic will also be of great value.

Proposals are solicited as to the types and forms of data that should be included in the comprehensive final report on the Pilot Project, and for identification of individuals to participate in drafting appropriate elements of the above report.

A global monitoring program of any nature required wide participation by Member States of the sponsoring organizations. Therefore participation of developing countries in the Pilot Project will be of great importance and value. We are very glad to note that a number of developing countries have expressed their interest in participating in the Pilot Project and have sent experts to this Symposium. It gives us a good opportunity to discuss and identify their training, education, and assistance requirements, in order to enable them to participate actively and, on the other hand, to indicate availability and terms of technical assistance that can be provided in training, training aids, laboratory facilities, experts, and consultants. I wish to note here that the Biological Laboratory at the Bermuda Biological Station for Research has already offered to arrange a training course for experts from the developing countries.

It should also be pointed out that the United Nations Environment Program has recognized the Pilot Project as an important step in developing a global monitoring system and has agreed to provide financial support for its development. This will enable us to accelerate the planning and operational phases and, in particular, to assist developing countries in their participation.

In conclusion, I wish you every success in your work during this week.

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Survey Analyses for Petroleum Derived Hydrocarbons in the Ocean

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As one of the major terminals of the oil transportation routes in the world, or as a country which greatly depends on fisheries activities, Japan has, of necessity, been solicitous about the actual state of marine oil pollution. In the most recent few years, some of the scientists who belong to the government organizations have exerted their efforts on the quantitative measurement of petroleum-derived oil in the ocean, although they have not yet achieved a sufficiently effective monitoring system at present. Here I will describe some of their activities as a basis for further discussion of marine oil pollution monitoring.

The Far Sea Fisheries Research Laboratory of Fisheries Agency has been conducting larva sampling in the Indian and Pacific Oceans as part of the tuna research project. Recently, particulate petroleum residues were found to exist in the collected samples, and in 1971 K. Nasu of the laboratory, and his co-workers, started to investigate the distribution of these residues in the oceans. Some 40 official ships, such as the fisheries training ships or the fisheries research ships, have engaged in the project and the same sampling method was employed for each ship. Larva nets of 1.4-meter diameter and 4-meter length were towed for 15 minutes at a speed of 2 knots (traversing a distance of about 900 meters). The amount of the particulate residues were represented by an arbitrary scale for the sake of convenience. Amounts were expressed as "Found" or "Remarkable" according to whether the amount was less or more than 1/4 of the sample surface in a 5-centimeter-diameter bottle respectively. Fig. 1 shows the distribution of the particulate residues in the ocean during the period from October 1971 to September 1972. According to K. Nasu and others, the particulate residues are abundant in the marginal area of major ocean currents such as the Kuroshio and the Indian South Equatorial Currents, and also along the major oil transportation routes (as was expected).

The daily patrol for the illegal discharge of waste oil has been conducted by the patrol boats and aircraft of the Guard and Rescue Department of the Maritime Safety Agency. Although the number of cases reported to the Department does not seem to be increasing since 1972, there are still a considerable number of occurrences-more than 2000 annually. In 1971 and 1973 the Department conducted a survey of tar balls that had drifted to the coast of Japanese islands, using its patrol boats, some 400 from local fisheries cooperative associations, and some 650 of trusted monitors. According to the survey, the greatest number of tar balls were found on the coasts of the South-west Islands and on the Pacific coast (Fig. 2). In the same period, the Department also conducted a sampling of tar balls by patrol boats along 18 fixed routes in the open sea around Japan. The sampling routes were chosen to take into account the shipping routes and the ocean current system. The sampling method was as follows: nets of 0.75 millimeter meshes, 1-meter diameter and 2-meter length were towed for some 500 meters at the speed of 2 to 3 knots, and the number of particles were simply counted. By this survey, it was found that a considerable amount of particulate residues of millimeter size are drifting in and around the Kuroshio current (Fig. 2) and that there seems to be no significant difference in amount between 1971 and 1973.

The Hydrographic Department of the Maritime Safety Agency has been conducting chemical analyses of petroleum hydrocarbons in sea water to study the present level of marine oil pollution, as part of the project monitoring the sea around Japan, together with analyses of petroleum hydrocarbons in the bottom sediments of major bays. The analysis was carried out by R. Higano of the Department and his co-workers, who took the saturated hydrocarbons (paraffin-naphthene) as an indicator of the petroleum hydrocarbons in the sea water or sediment. The distribution of petroleum hydrocarbons obtained from their 1973 analysis are shown in Fig. 3. The chemical procedure employed in these analysis is as follows: Samples were condensed after extraction with n-hexane, treated with alkali-alcohol solution, charged to a column of activated silica gel and alumina, and diluted with n-hexane. The paraffin-naphthene in the first 20 ml was freed from n-hexane, weighed, and analyzed by a gas chromatograph.

The same group analyzed surface, subsurface, and bottom (sediment) samples, which were taken at each of some 18 stations in Tokyo Bay, to see how the discharged petroleum was distributed into these portions of the Bay. In this study, the surface oil samples were scooped by a stainless steel net (30 mesh, 40 x 40 cm) and then dissolved into n-hexane, and the bottom samples were collected by a Smith-McIntyre Grab and treated for one hour with alkali-alcohol solution in a steam bath before extraction. According to their estimation 1 to 10^{-1} tons of petroleum were on the surface of the Bay, 10^2 tons in the water body and 10^3 tons in the bottom surface layer of 10-cm thickness, and it was clear that the accumulation of waste petroleum in the bottom sediment was very important, especially in shallow waters.

In view of the above mentioned activities in Japan, it is considered that many non-research ships and many men who are not marine sampling specialists, must be involved for effective marine pollution monitoring of wider areas; it is also clear that the techniques used must be the same for each sampling, and the simpler the techniques, the better. To meet such requirements, the techniques and instruments should be developed by scientists. Further, to make monitoring more effective and to make data interpretation easier, studies, such as on the calibration and accuracy evaluation of the simplified techniques, and the oceanographic and meteorological studies of the monitoring areas, must also be done by scientists. The scientific basis for such needed studies is expected to be discussed during the Symposium.

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Analysis Standards and Intercomparison of Data

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Please consider this brief talk in the nature of a footnote rather than anything larger since most of the topic that I am going to touch on today was discussed extensively yesterday and this morning. However, even though pouring oil on troubled waters is no longer fashionable today, I would like to ruminate for a moment or two on the topic of analysis standards and the intercomparison of data, even at the risk of some repetition. I would like to place this topic in a broader context in the hope of shedding a little more light on a problem area that has been noted for the amount of heat it has generated in the past.

The objective of this symposium is to discuss the status of marine pollution monitoring and the progress that is being made. Both aspects of this symposium are parts of a larger area, the area of environmental protection. I believe, however, that we cannot stop with environmental protection as the ultimate goal; instead we need to perceive environmental protection and all that it subsumes in an even larger context, as an important part of a larger effort to improve the quality of life of all nations.

While environmental protection obviously is an essential requisite for maintaining and enhancing the life support system for man, it is only one factor in the quality-of-life equation. In addition to the need to maintain life itself, we need a sound economic basis to provide the goods and services which yield the amenities of life, such as food, clothing, and shelter, adding the dimension of quality to human existence. The balance between the need for environmental protection, including marine pollution abatement and the need to maintain a nation's economic health is a delicate one indeed, and the maintenance of that balance depends to a large extent on our collective success in identifying and correctly diagnosing pollution problems as well as in prescribing reliable, cost/effective corrective measures. Both diagnosis and correction in turn depend heavily on our abilities to accurately measure and monitor ambient environmental conditions and on our success in characterizing marine pollutants and their sources.

The development of rational and justifiable pollution abatement regulations must be based on three essential criteria. First, accurate and reliable scientific information and data in sufficient amounts to permit the development of rational hypotheses and conclusions regarding the status of the environment; second, the availability of demonstrably feasible monitoring and control technology; and third, the availability of a system for selecting cost/effective options for solutions. However, in order to meet all three criteria, we must develop standard measurement methodologies and practical means for the intercomparison of data.

This is especially important in attempting to cope with marine pollution, not only because of the ubiquity of the oceanic environment, but because of the practical impact of pollution controls on international commerce. The degree of harmonization of international trade will depend to a large extent on our success in gaining international acceptance of standard measurement methodologies as well as in achieving intercomparability of environmental measurement data on an international level.

The Stratton Commission Report to the President of the United States in 1969 stated that, "At present, there is a wealth of data within the nation that is of limited value because of low confidence in the data quality or because the data came from diverse sources and are not comparable. This is not only a national problem, but it is increasingly becoming an international one." Today, of course, it is recognized as an international problem which has fully matured. Fortunately, the numbers of laboratories and other institutions, both governmental and private, have increased, so we are in a better position to cope with the problem than we were back in 1969.

For example, within the Department of Commerce, as you have undoubtedly heard, there are two national facilities that have unique responsibilities and capabilities for helping to assure data quality and comparability. One is the National Bureau of Standards which is responsible for maintaining the national standards of measurement for international agreements on standards and for disseminating methods of achieving accuracy and comparability in measurements wherever they are made. The other is the National Oceanographic Instrumentation Center under the National Oceanographic and Atmospheric Administration which serves as a national focal point for oceanographic instrument evaluation for recommended calibration procedures, for advice on instrument performance needs and specifications, and for coordinating data as part of intercomparison programs. Together, these laboratories and others like them in other countries can do a great deal to help rectify the situation described in the Stratton Report so succinctly, a situation which unfortunately still exists. These laboratories are natural collaborators with advantages to each. NBS furnishes expertise on the basic standards of measurements which can be utilized by the NOIC. NOIC, in turn, provides a familiarity with real oceanographic measurement problems and thus becomes the interface between the National Bureau of Standards and the oceanographic research community in assuring traceability of oceanographic measurements to national and international standards among its other functions.

In the past, contact between these laboratories has been largely informal in the sense that collaboration has been between professional scientists and engineers in the two organizations. Hopefully, a more formal arrangement can be worked out to facilitate the development of jointly funded programs.

Recently, an interagency committee was chartered by the Secretary of Commerce to advise the NOIC on priority needs of Federal agencies engaged in oceanographic measurements. NBS has membership on that committee. At present, the Committee is working with NOIC on a policy statement, to be presented to the Interagency Committee on Marine Sciences and Engineering, that will urge all Federal agencies in the United States to work actively with the National Oceanographic Instrumentation Center of NOAA to provide jointly accepted procedures for instrument performance evaluation and for instrument calibration procedures and schedules. We hope that user agencies will actively participate in data intercomparison programs as well.

Now, what about the rest of that quote from the Stratton Commission report, "...the wealth of data that is of limited value because of low confidence in the data quality." Here, again is an opportunity for the Department of Commerce, through its National Bureau of Standards, to make vital contributions. Within NBS, the Office of Standard Reference Data undertakes critical reviews of measurements and data in fields of national priority. These reviews can be done either in-house or by outside experts through contracts. The product of such a review is ordinarily a careful evaluation of an existing body of data, raising it from a low to a high confidence level, resulting in the retrieval of substantial (and often expensive) data from the archives for a more general, practical use. It is my hope that NBS will be encouraged to develop high priority data evaluation programs pertinent to marine pollution research. Of special interest today because of the growing availability of modeling techniques is the reliability assessment of the measured kinetic and transport parameters that govern the movement of pollutants from sources to the oceans.

Let me conclude by suggesting that there are two basic high priority program areas in which progress will depend on the further development of international cooperation. One is the establishment of environmental base lines, and two, the investigation of the biological effects of oceanic pollutants. The great variety of marine and estuarine environments as well as the tremendous diversity of biological species mandate the development of workable multinational instruments for scientific cooperation. Progress in these areas of cooperation will depend as heavily on the utilization of intellectual resources as well as on measurement and monitoring technology. Fortunately, the intellectual resources are available in most countries for the task at hand. Success can be achieved if scientists and technologists will organize well-coordinated international programs for attacking the measurement, monitoring, and intercomparability of data problems. It is my sincere hope that this Symposium signals the beginning of the attack.

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Maritime Consideration of Oil Transportation

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It is a pleasure to be with you today and I welcome this opportunity to participate in this symposium on Marine Pollution Monitoring. I was particularly gratified to see that the program principals include 14 distinguished ocean research scientists from other nations. For I believe that we all will agree that pollution of the marine environment is an international problem and can best be solved by preventive and remedial measures launched on an international front.

While the pressures to institute marine pollution abatement measures are particularly strong in the United States, it is also readily apparent that there is a mounting universal demand that effective corrective actions be taken to protect the marine environment.

Here in this country, all concerned parties recognize that the most effective way to attack marine pollution problems is by international regulations and standards. However, there is also a strong belief in some quarters that if such regulations are watered down, or subjected to unacceptable ratification delays by other nations, the United States should unilaterally impose stringent regulations to protect its coastal zones, shorelines, and waterways from ship-generated pollution.

This is apparent from the fact that Congress has already enacted one law -- the Ports and Waterways Safety Act of 1972 -- calling for unilateral pollution abatement measures which clearly reflected its dissatisfaction with the lack of effective international standards. It should be noted, however, that this law was enacted prior to the 1973 IMCO Convention which focused on marine pollution abatement measures.

Before going into some of the specific factors and initiatives reflected in our programs, I think it is important to provide this audience with some perspective of the size of the American-flag tanker fleet in relation to the world tanker fleet.

The American-flag fleet comprises 240 tankers aggregating 7.8 million deadweight tons, equating to 5 percent of the number of tankers in the world fleet, and less than 4 percent of the collective world tanker tonnage. It also should be noted that foreign flag tankers transport about 95 percent of this nation's oceanborne petroleum imports. Because most of our tankers are of relatively small sizes, averaging only 32,500 dwt., they are generally uncompetitive in our foreign trade, and operate nearly exclusively in our domestic trades and in the carriage of government-controlled grain cargoes.

However, under the Merchant Marine Act of 1970, there is an ongoing shipbuilding program to bring about a reentry of American-flag tankers into our foreign trade. Since the enactment of this law, 30 crude and product tankers for foreign trade operation have been ordered from American yards, 26 of which remain to be delivered. We also are building 27 additional tankers for domestic operations. The total tonnage of these foreign trade and domestic trade tankers is 4.5 million dwt., which is still a relatively small percentage of the 219 million deadweight tons of tankers currently under construction, or under contract, in the world's shipyards.

Our goals are to achieve the complete elimination of intentional polluting discharges from ships by 1975 if possible, but certainly by the end of the decade, and the minimization of accidental spills. We also believe that these goals should be pursued through cost-effective measures which will not impose discriminatory competitive burdens on the American-flag fleet.

Our programs are influenced by in-house studies and initiatives dealing with pollution prevention, as well as several laws enacted by the Congress and existing and proposed international regulations to curtail ship-generated pollution.

In terms of MarAd's (Maritime Administration) initiatives, since 1965, all vessels built with construction-differential subsidy must conform with the agency's Standard Specifications for Merchant Ship Construction. In 1971, as a result of mounting concerns about the marine environment, Section 70 of these specifications, covering Pollution Abatement Systems and Equipment, was revised to meet existing standards and certain anticipated future national and international regulations. Section 70 has been periodically updated to meet U.S. Coast Guard, EPA, and IMCO standards.

Among the compulsory requirements stipulated by Section 70 are an oil-content meter to monitor ballast and bilge discharges, an oil-water separator to process such discharges, tank size limitations, and a sewage treatment plant.

Four laws in particular have had a major influence on our pollution abatement programs:

(1) The National Environmental Policy Act of 1969

(2) The Water Quality Improvement Act of 1970

(3) The Federal Water Pollution Control Act, as Amended in 1972, and

(4) The Ports and Waterways Safety Act of 1972

The National Environmental Policy Act of 1969 directed all agencies of the Federal government to utilize a systematic, interdisciplinary approach in the planning and decision-making which may have an impact on man's environment. In implementing this approach, the Act requires all Federal agencies to prepare an environmental impact statement on proposals for legislation or other major Federal actions that may significantly affect the quality of the environment.

As a result of the shipbuilding program generated by the Merchant Marine Act of 1970, MarAd has either issued, or is currently in the process of issuing, several environmental impact statements which fulfill the obligations of the National Environmental Policy Act.

The most significant and well-known of the MarAd environmental impact statements is the one dealing with our subsidized tanker construction program.

In accordance with a court-approved stipulation agreement dated January 8, 1973, resulting from litigation action brought by the Environmental Defense Fund, Natural Resources Defense Council, Inc., and the Center for Law and Social Policy, the Maritime Administration issued a Final Environmental Impact Statement on May 20, 1973. In addition, we prepared an Economic Viability Analysis of eight different features which the plaintiffs felt would make MarAd's subsidized tanker program more compatible with the environment.

These features included such items as twin propellers, and controllable-pitch propellers for better vessel control, double bottoms and double sides to prevent oil spills in case of accident, and flue-gas tank-inerting systems to prevent explosions. Also analyzed were reductions in the size of individual cargo tanks to minimize oil discharge in case of damage, lateral thrusters - forward and aft - for better maneuverability, and totally segregated clean-ballast systems to minimize oily ballast waste.

Subsequent to the issuance of the Final Environmental Impact Statement, the Maritime Subsidy Board on August 30, 1973, issued a Final Opinion and Order on the Tanker Construction Program. Some of the essential conclusions and findings of this Subsidy Board Docket were:

(1) Present and future vessels receiving construction subsidy shall be in strict compliance with MarAd's tanker pollution-abatement specifications and a specification providing for collision-avoidance radar;

(2) All tankers in excess of 100,000 dwt. receiving government aid shall contain inert gas systems in the absence of a satisfactory reduction in tank sizes;

(3) MarAd will continue to participate in, and support, IMCO and U.S. Coast Guard efforts to devise major anti-pollution design and equipment features for tankers and to incorporate into government-aided contracts such anti-pollution features established by the 1973 IMCO Marine Pollution Conference and/or Coast Guard regulations;

(4) MarAd training programs will include anti-pollution training manuals and course materials for tank vessel operation; and

(5) MarAd will intensify its research and development activities to improve technology in combating marine pollution with respect to the operations of oil-carrying vessels.

Other environmental impact statements that MarAd is involved in are:

(1) An environmental impact statement on the MarAd Chemical Carrier Program. A draft statement on this subject was issued on March 15, 1974;

(2) An environmental impact statement on the MarAd Title XI Program Vessels Engaged in Offshore Oil and Gas Drilling Operations. The draft statement on this program will be issued early this summer;

(3) A Proposed Shore Facility for Treatment and Disposal of Ship Generated Oily Water Wastes. The Final Environmental Impact Statement for the facility was issued on November 27, 1973;

(4) An environmental impact statement on our Nuclear Ship Program which is currently being developed under contract to the NUS Corporation.

To return to the U.S. laws which impact on marine pollution, the Water Quality Improvement Act of 1970, enacted in April of that year, stipulates that it is the policy of the United States that there should be no discharges of oil into the navigable waters of the United States, upon adjoining shorelines, or into the waters of the contiguous zone which cause a visible sheen or discoloration of the water. (A visible sheen informally is defined as 10-20 ppm of oil.)

The Federal Water Pollution Control Act, as amended in 1972, declares the national goal of "complete elimination of discharge of pollutants in our navigable waters by 1985 and an interim goal of water quality providing for the protection of marine resources, wildlife, and recreation by July 1, 1983." The Act provides for the imposition of financial liability for the discharge of pollutants from vessels or shoreside facilities. It also authorizes the EPA to set standards and promulgate regulations for the performance of marine sanitation devices aboard vessels.

Finally, the law which may have the greatest impact on the Tanker Construction Program is the Ports and Waterways Safety Act of 1972. Under this law, the Coast Guard was authorized to insure the safe movement of vessels in congested port areas by controlling vessel traffic. It also authorized the Coast Guard to promulgate rules and regulations for tankers entering U.S. waters, setting forth minimum standards of design and construction of tank vessels for the purpose of protecting the marine environment. Such rules shall also set standards designed to improve vessel maneuvering and stopping ability and to otherwise reduce the possibility of cargo loss in the event of accidents, and to reduce pollution by normal vessel operations, such as deballasting, cargo handling, and other activities.

While such rules and regulations were promulgated, they were held in abeyance to ascertain IMCO's consideration of recommendations for international standards last fall. It is understood that the Coast Guard will issue construction and operating standards for U.S. flag coastwise tank vessels which will become effective on July 1 of this year.

MarAd has played an increasingly significant role in supporting U.S. international efforts by its participation in IMCO activities and by developing back-up economic and technical studies in support of the U.S. Anti-Oil Spill policy initiated by President Nixon in his message to the Congress of May 20, 1970. This message called for effective multilateral action by international bodies, such as IMCO, to prescribe international standards for the construction and operation of tankers.

The U.S. Anti-Oil Spill Program was given further impetus by then Secretary of Transportation Volpe's pronouncement of "zero discharges" of oil by mid-decade. The NATO/CCMS Conference Resolution, subsequently adopted as the goal of the 1973 IMCO Marine Pollution Conference, fell short of the original U.S. position, but called for work to start at once to achieve by 1975, if possible, but not later than the end of the decade, the elimination of intentional pollution of the seas by discharges of oil and oily wastes.

Prior to the 1973 IMCO Marine Pollution Conference, the original concept of "zero discharge" meant no discharge, or zero parts per million (ppm). However, this was considered by industry as unrealistic and unattainable under present day technology.

The 1973 IMCO Marine Pollution Convention replaced the "zero discharge" concept with "zero polluting discharge," which was defined as 15 ppm, or no visible traces, of oil. The more realistic approach taken by the 1973 Convention gave us a little more room to work with. As one can recognize, however, the cost to achieve 15 ppm is still substantial and, therefore, it is felt that additional research is needed to confirm the need for such high standards.

Nonetheless, the requirements adopted by the 1973 IMCO convention are considered by the U.S. to be, in the most part, cost-effective and realistic. Besides establishing the "no discharge" zone of 50 miles from land, the Convention required new tankers to be designed with segregated ballast capabilities and all existing tankers to be fitted with a Load-On-Top System for handling oily ballast and tank washings.

In addition, a new IMCO committee has been established, the Marine Environment Protection Committee. This Committee has been given the responsibility for handling all future marine pollution issues for IMCO. It is the intent of the Committee to shorten the traditionally laborious task of amending and issuing new international pollution control standards.

IMCO has also recognized the importance of the development of scientific information, such as that being discussed at this symposium and workshop. Resolution 12 of the 1973 IMCO Marine Pollution Conference specifically calls for the "Development of Scientific Information on Water Quality Criteria."

MarAd is firmly committed to the policy that strong and effective pollution control regulations can go a long way towards protecting the marine environment. However, before rigid standards can be established, we believe a definitive basis must be developed which indicates the need for such standards. This is particularly true when high pollution control standards require costly and sometimes unrealistic construction and design requirements for vessels.

It is the hope of the Maritime Administration that this symposium and workshop will help establish and formalize the techniques and standards required to determine the actual fate and effect of oil spills or discharges into the marine environment. Such standards are needed to establish a baseline of data that will be the basis for realistic requirements.

With the development of baseline data and uniform measuring techniques and procedures, effective control devices can then be designed and manufactured to protect the marine environment from vessel source pollution.

In this area, MarAd has initiated two studies, discussed during the course of this symposium, which are designed to develop a data base for future practices, and regulations regarding the control of marine pollution.

The basic objective of these two projects is to establish a body of hard knowledge and basic data in order to determine, with some degree of scientific precision, the level of oil in the open oceans and the amount of oil contained in ship discharges considered to be harmless to the marine environment. We feel that the establishment of baseline information will permit a more rational approach to the formulation of realistic and meaningful standards for permissible oil discharges from ships.

Our first program, initially set up with ESSO Research and Engineering in June 1972, was designed to collect and analyze ocean samples to determine background hydrocarbon levels in the ocean waters. Data developed from this study showed that extremely low hydrocarbon concentrations existed in surface and subsurface waters.

Subsequent to the completion of this particular project, ESSO Research and Engineering has required and received additional funding from NOAA, with funding support from MarAd, to extend its ocean sampling program in the Pacific Ocean, concentrating on the Port Valdez to West Coast routes.

Another program which has been co-sponsored by the same three agencies sponsoring this workshop, NOAA, NBS, and MarAd, is the Fate and Effects Study on the Scientific Aspects of Oil Discharges in the Marine Environment.

This program, although somewhat hindered by funding cutbacks, originally called for a study to establish the fate and effects of oil discharges on the marine environment and to use this information to form the basis for the establishment of meaningful standards. Several of the papers given here have been the direct result of this project.

It is apparent that the work of this group to develop techniques for the monitoring of marine pollution is very pertinent to the goals of the Maritime Administration, as well as to other agencies and organizations represented at the workshop. As indicated by the wide range of papers from the various areas of interest, i.e., government, industry, and academia this subject is undergoing a very thorough research effort.

I am hopeful that the activities of this symposium will result in the development of working guidelines for marine pollution monitoring that will significantly advance the objective of producing oil tanker equipment and systems that will effectively protect the marine environment at a reasonable cost.

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Marine Pollution Data Archiving and Exchange

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Environmental Data Service, NOAA

In 1961, at its formative session, the Intergovernmental Oceanographic Commission of UNESCO established its first standing working group, the Working Group on International Oceanographic Data Exchange (IODE). Only a year earlier, United States ocean scientists had appealed successfully to their National Academy of Science and to the Legislative and Executive Branches of Government for the establishment of a national oceanographic data center. I cite these two examples to indicate that only ocean scientists and coordinators of ocean science programs are concerned with effective exchange of oceanic data. In keeping with this philosophy, I will speak to you today on the subject of effective international exchange of marine pollution data.

In 1970, the Working Committee, IODE, at its fifth session, considered the first and second reports of the Group of Experts on the Scientific Aspects of Marine Pollution (GESAMP) and their expressed desire for the establishment of arrangements by which all data pertaining to marine pollution could be suitably stored in the world or specialized data centers. The Group of Experts on the Long Term Scientific Policy and Planning proposed a program for the Global Investigation of Pollution in the Marine Environment (GIPME) and a data information and management system to accompany that program. Following this, the chairman of GESAMP addressed correspondence to the chairman of the Working Group IODE, expressing his concern for the capabilities of the national and world data centers to adequately archive and exchange marine pollution data. Added to these concerns, was the concern of the pre-Stockholm Conference Meetings of the Intergovernmental Working Group on Marine Pollution (London 1971) and the Intergovernmental Working Group on Monitoring and Surveillance (Geneva 1971) as related to data and information exchange. Late in 1971 and prior to the Stockholm Conference these considerations resulted, at the Sixth Session of IODE, in the establishment of an _ad hoc_ Group on Marine Pollution Data. The terms of reference of this group include:

"a. The _ad hoc_ Group will identify types of data which should be included routinely in the category of marine pollution data for international exchange, and the feasibility for automatic processing of such data. Other pollution data and relevant information not amenable for international exchange should be identified and proposals made for an adequate referral system for them. Recognizing that there are problems in the lack of standardization in some categories of marine pollution data, the Group should study and recommend the ways in which such data could be made available for international exchange; and

b. The _ad hoc_ Group should recommend a means by which marine pollution data, identified as to the foregoing, already stored in various archives can be appraised as to their availability for uses such as baseline studies and trend analyses. Sources of such data would include various regional, national, international and other archival and research institutes. The Group should also take into account the potential role of national coordinators for marine data management."

There is a common tendency for scientists who come together to talk about data and data exchange to spend considerable time and effort speaking to the problems and interests of their science before they can settle down to addressing the matter of data exchange. This tendency is completely understandable and, of course, provides the necessary perspective in which the matter of data exchange must be clearly viewed; that is, if effective exchange is to be arranged, the full cooperation of the scientist is a vital matter.

It was in this vein that the U. S. member of the IODE ad hoc Group on Marine Pollution Data, supported by the Director of the U. S. National Oceanographic Data Center and the National Science Foundation's Office of the International Decade of Ocean Exploration, called a workshop of prominent analytical marine chemists to discuss these matters in July 1972. The results of this workshop were incorporated into the report of the ad hoc Group as presented to the IODE at its Seventh Session, United Nations, New York, 1973.

In brief, the Workshop agreed that free and effective, rapid exchange of marine pollution data, including micro-contaminant chemistry, was possible only in those instances where there were internationally accepted standards for sampling, measuring, calibrating, etc. Only in such cases could the measured value of the concentration of a chemical constituent stand alone as a numerical value having meaning to other scientists and users of the data. Only then could such numbers be usefully placed into a central data bank, merged, and then used to produce summary products such as horizontal and vertical distributions, trend analyses, or other statistical products. The Workshop also agreed that, at the present time, there were no chemical measurements in the ocean that enjoyed this status, (with the possible exception of salinity and nutrient chemistry, for which reasonably well-accepted analytical techniques and standards permit the meaningful direct exchange of numerical values on chemical constituent concentrations, that waiting several years for the assemblage of data and subsequent publication of selected data was an alternative which could be improved upon. Even so, the scientific literature will probably remain the only viable alternative for promulgation of research data from those experiments that are at the fringe of analytical technique or instrumentation development. But it was further suggested that, in most cases, it would be possible to improve upon these alternatives by extensive documentation of the basic data set. Documentation as to sampling material and technique, shipboard fixation methodology, the time delays between sampling and fixation, identification of analytical methods, and instrumentation including shipboard and laboratory standards were but a few of the dozens of documentation items suggested by the Workshop. Thus, a numerical data set accompanied by such documentation would permit any of a variety of secondary users, scientists, managers, and citizens, to evaluate and draw their own conclusions as to the usefulness of a particular data set for a particular purpose.

The strength of this approach becomes apparent when one realizes that similar documentation, accompanying not only data sets but simple inventories of data, can provide for archiving of inventories in addition to or in place of archiving of the actual data. Thus, two additional advantages accrue. First, such documented inventories of marine chemistry data may be automated readily, be made fully searchable, and be extremely useful as a data referral tool. This is specific and documented referral, thus reserving the time and cost of full exchange to those instances where the usefulness of such an exchange is evaluated in advance. Second, such documented inventories may readily serve as a means by which earlier files of unpublished or only partially published observational data may be brought to light in an organized fashion available for the review of today's concerned ocean community, and evaluated for possible selective accessioning into a baseline file. Such an approach has been recommended by the IODE ad hoc Group on Marine Pollution Data and approved by the parent Working Committee IODE and the Intergovernmental Oceanographic Commission.

Subsequently, in January of 1974, national coordinators for International Oceanographic Data Exchange were asked to contact their nation's scientists and program managers involved in marine pollution research and monitoring to implement a pilot system of documented inventories. This early pilot effort may use any system meeting the goals of a documented or second-level inventory. The Report of Observations/Samples Collected on Oceanographic Programs (ROSCOP) is considered a first-level inventory, not a second-level inventory such as we suggest here, but both the IOC/SCOR ROMBI form (that is, Report of Marine Biological Investigations) which contains an extensive pollution section, and the U. S. Environmental Data Index (ENDEX) inventory systems, which have been introduced into the IODE, have potentials for this use. Such inventories would be accompanied as would any actual data transmission, by documentation which would include specialized information such as that recommended in the first report of the ad hoc Group on Marine Pollution Data, and, hopefully, any additional documentation that may be suggested by this group in the workshop which follows later this week.

No reports are yet back from the National Coordinators for International Oceanographic Data Exchange, but I am aware of several countries where this matter is presently being considered in relation to the developing IGOSS Marine Pollution Monitoring Pilot Project. To assist in this effort, I, and several of my international colleagues, will join the pollution scientists and managers participating in the workshop convening tomorrow.

There are two other ad hoc Groups of the IODE Working Committee who share our interests in these matters. These are the ad hoc Group on Format Development and the ad hoc Group on IGOSS Data Archiving and Exchange. The former group is concerned primarily with establishing optimum formats for fully processed and carefully validated data sets which will form the long term permanent archive. The latter group is concerned primarily with procedures and formats for archiving and exchange of IGOSS data which have either been transmitted over the international telecommunications system, or for which re-dissemination or data products are short term services. There has been insufficient advance in the work of my ad hoc Group to permit us to make any specific recommendations to the IODE format development group.

However, we have continuing close liaison with the work of both of these ad hoc groups. In this regard, the deliberations and considerations of this joint meeting of the IOC and WMO scientists will serve as a sound basis upon which to advance the work of all three IODE subsidiary bodies.

For those of you remaining to participate in the workshop which immediately follows this symposium, I actively solicit your constructive support of the present and future work of these groups. For the longer term, I further solicit your active support and continued cooperation through your national coordinators for the IGOSS Marine Pollution Monitoring Pilot Project, your national coordinator for IGOSS and your national coordinator for International Oceanographic Data Exchange. We are privileged to have with us to participate in the workshop, the Director of the Federal Republic of Germany's National Oceanographic Data Center who is his nation's coordinator for both International Exchange of Oceanographic Data and for the Pilot Project; Mr. Jaquiam Ros of Spain who is a member of my ad hoc Group on Marine Pollution Data and his nation's coordinator for the IGOSS Marine Pollution Monitoring Pilot Project; Mr. Thomas Winterfeld, Chairman of the IODE ad hoc Group on IGOSS Data Archiving and Exchange; and Mr. Robert Ochinero, the U. S. National Coordinator for International Oceanographic Data Exchange and Director of the U. S. National Oceanographic Data Center. I hope you will indeed assist us in this aspect of the IGOSS Marine Pollution Monitoring Pilot Project.

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Biological Environmental Effects

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At the discussion this morning, there was quite a bit of intermingling of matters concerning both monitoring and effects of contaminants. I would like to make it clear that I agree with Dr. Ehrhardt that effects are a separate matter, something that is quite distinct from the monitoring. Nevertheless, I feel quite strongly that there must be a continuous dialogue between people carrying out the research on effects and the people who are planning and carrying out the monitoring activities. I will have more to say about this before I am finished, but first I want to talk about our program on effects at our Northwest Fisheries Center.

This program got underway shortly after NOAA was established as an agency in 1970. At that time, we had had some work going on along this line, particularly by Bob Clark, in connection with monitoring the content of petroleum hydrocarbons in marine organisms in Puget Sound, but about two and a half years ago, we set up an environmental conservation division to which we brought Bob Clark and his program and to which I brought from the utilization side of the old Bureau of Commercial Fisheries a group of chemists. This became the first nucleus of our environmental conservation activities. We soon were supplied with other scientists with different disciplinary backgrounds, such as biologists, physiologists, geneticists, and microbiologists. Today we have a staff of about 30 scientists who are able to undertake work on the different aspects of our program from different points of view. We have the program arranged in three units so we can approach things from different standpoints.

In the first unit, which consists mostly of chemists, we are looking at how the contaminants enter the fish, either through the food or through the water, and how the contaminants distribute themselves around the body of the fish; how they interact; the mechanisms by which they bring about harm at vulnerable sites, and then something about how they might be metabolized so that they are eliminated by the fish's defense mechanism.

In the second unit, we are looking at the behavior of fish, mainly from a physiological standpoint. We are more concerned with long term chronic effects than just the lethal effects. We are looking at such things as the effects of contaminants upon the disease resistance of fish, the effects upon sense organs, and other types of effects.

In the third unit, we are looking at how fish behave in their natural environment. We have several field stations where we are able to compare the results of some of our laboratory investigations with what goes on in the natural habitat.

We are undertaking this work to ascertain long term chronic effects rather than lethal effects. I would like to tell you about one project in which the technique being used is a little bit different than those being used in any other part of the world with which I am familiar. This project is being carried out by Dr. Roubal of our staff and it involves something called spin labeling. It is being used to look at what goes on at the membrane level and subcellular parts of fish. We have chosen this because it is at the membranes that many of the enzymes and other types of activity which can be interferred with by contaminants that enter the fish operate. Spin labeling is a new technique that was developed at Stanford University about five years ago. Primarily, it has been used in the field of medical research; we are among the first to use it in marine science. It is a very simple technique and yet one which gives considerably more information than the analogous radioisotopic tracer techniques because it shows not only the presence of the tracer, but also in what kind of an environment it is located. It is especially useful to be able to look at what is happening at subcellular levels because we can tell whether the contaminants go to the surface of membranes, whether they penetrate the membranes, or whether they are associated with lipids, proteins, or other factors. The technique has been used in our studies so far only for examining how salmon pick up and distribute contaminants obtained through their food. Later we will extend the use of this technique to other aspects and other species. My discussion here will be restricted to salmon and their ingestion of hydrocarbons through their food.

In a general way, this work is carried out very simply by feeding separate hydrocarbons to the salmon for different experiments. Then all we have to do is examine the part of the fish that we are interested in. We have been using spinal cords because we feel that contaminants have the greatest potential for harm when they enter the neural systems. We dip the spinal cords in a solution of the label, then place the specimen in the instrument, and immediately get a chart that gives us all the information that we need to know.

We are using several types of labels (Fig. 1) which also have been used in medical research. Each has a nitrous oxide group that contains the free radical that sends back the information. They are attached to different types of compounds that will penetrate membranes to different distances from the surface, either remaining on the surface or going just beneath the surface or to the center.

Figure 2 shows such a label penetrating at the upper right portion into the center of a membrane. The center of the membrane is a sort of a fatty, lipid material. Figure 3 shows the type of curves we get. The top curve is the spectrum for a label without any contaminant present; this label is directed into the interior of the membrane. The curve below shows the type of curve that appears when an aliphatic hydrocarbon has been fed to fish and then is placed into the instrument. The two curves tell us that the aliphatic type of hydrocarbon has gone to the center of the membrane. If, however, we had used a fish that had been fed with aromatics, we would have gotten a curve identical to the one shown at the top, indicating that aromatics do not go to the center of the membrane.

In Figure 4, we have a labeled membrane in which the label is directed to the surface of the membrane. Here, if the fish has been consuming aromatics, we get the different type of curve (shown at the bottom) indicating that the aromatics are at the surface of the membrane, but if we had used fish fed aliphatic hydrocarbons, there would have been no change, showing that the aliphatics were not at the surface, but at the center.

In further studies using radioisotopic tracers, we have shown that the aliphatics which occur at the center of a membrane can be gotten rid of quite rapidly, but not completely. Within about a month's time, the values fall to about 10 percent of their original value, but after this period of time, they continue steady for many months for as long as our experiment has lasted. The aromatics, on the other hand, which occur at the surface of the membrane, disappear almost at once; within two or three days they have reached undetectable limits. We believe this is because they are in the presence of enzymes which can very rapidly purge them.

This is a very rapid technique. We expect to expand its use to other species of fish and to hydrocarbons which enter the fish not only through the food but also through the water.

We have other programs too numerous to mention here. These include examining the effects of hydrocarbons upon the sense organs of fish. Some of our preliminary findings are that there seems to be an interference with the olfaction activity, but not with the lateral line in fish.

We are, at present, planning an expansion of our activities by a cooperative program with Environmental Research Laboratories, another agency within NOAA that has a facility at Seattle, and we hope, perhaps by the next fiscal year, to be carrying out a considerably larger program in cooperation with that agency.

Now, I would like to come back to this matter of cooperation and dialogue between people who are carrying out the monitoring programs and those who are carrying out the type of activities that we engage in at Seattle. About three years ago, I attended a meeting during which I listened to the discussions about monitoring programs to be carried out. Finally, I spoke about how we should also consider the matter of effects upon the fish of the things that were being monitored. I was told that the first thing that had to be done was to find out where the contaminants went in the water, and that this would take about 10 years, and that I should come back in 10 years and then we could discuss what needed to be done with respect to the effects. Now, I felt very strongly then as I do now, that this is not the way to approach the matter; that monitoring is not an end in itself. It has to be done, keeping in mind that the monitored contaminants may be harmful to the environment. In the National Marine Fisheries Service, we are concerned with what happens to the fish. Therefore, we are concerned about whether enough of the ideas of the people working on biological effects are being introduced into the thinking of the people planning the monitoring. I noticed yesterday that, in one of the discussions on collection of surface waters, they were talking about taking samples to a depth of one meter. I feel that this is a good example where, from the standpoint of the biochemists and the biologists and the biologists and the people looking at the effects of contaminants, we should know much more about what happens in the first two or three centimeters because, under some circumstances, eggs of fish are floating at the surface, and at the surface there is much higher concentration of contaminants than there is at a depth of one meter. So, it is this type of information I think we need to pass back and forth between these two groups so that the work that is done will be much more meaningful.

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Maritime Considerations

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International Convention for Prevention of Pollution from Ships

After two years of concentrated effort, the International Convention for the Prevention of Pollution from Ships was adopted by the IMCO Conference on Marine Pollution held in London, October 8 to November 2, 1973. This Conference, attended by 665 delegates from 79 countries, U.N. Agencies and intergovernmental and non-government organizations adopted the 1973 Convention, consisting of twenty Articles and five Technical Annexes. In addition, the Convention adopted the Protocol Relating to Intervention on the High Seas in Cases of Casualties Involving Marine Pollution by Substances other than Oil. The Convention further adopted twenty-six Recommendations and Resolutions.

This was a true landmark achievement in responsible intergovernmental cooperation and a significant step forward in achieving high pollution control standards on an international basis. The 1973 Convention will enter into force 12 months after it has been ratified by not less than 15 States, the combined merchant fleets of which constitute not less than 50% of the gross tonnage of the world's merchant shipping. Upon its entry into force, the present Convention will supersede the 1954 International Convention for the Prevention of Pollution of the Sea by Oil and the 1962, 1969 and 1971 amendments thereto.

The 1973 Convention will be forwarded to the U.N. Conference on the Law of the Sea to be convened next month so that it can be taken into account by the Law of the Sea Conference.

The main objective of the 1973 Pollution Conference was " . . . the achievement by 1975, if possible, but certainly by the end of the decade, of the complete elimination of the willful and intentional pollution of the seas by oil, and noxious substances other than oil, and the minimization of accidental spills . . ."

To a large degree if the provisions of the Convention are implemented on a worldwide basis, that objective has a good chance of being achieved. There are, however, some difficulties that must be overcome if the provisions are to be effective. First, and quite naturally, the Convention must come into force and be complied with and enforced to achieve the desired reduction in pollution. Secondly, the provisions must be feasible of achievement. While, for the most part, the provisions adopted by the 1973 Convention are considered cost-effective and realistic, there may be certain provisions of the Convention which will be difficult to achieve. I would like to focus my discussion on two examples which I believe fit this category. Further, I believe the examples I have selected in this regard are close to your interests. One of these relates to construction standards, the other to operational discharge standards. Following each of these I would like to discuss what the Maritime Administration is doing to overcome these difficulties.

Maritime Administration Role in Pollution Prevention

The main thrust of the Maritime Administration's (MarAd) program is in the prevention of oil pollution through cost effective measures which will maintain the competitive position of the U.S. merchant fleet. MarAd's program is based on the achievement of National goals in coordination with other government agencies and with the commercial organizations with which the agency deals. MarAd's main governmental coordination concerns the U.S. Coast Guard, the Environmental Protection Agency, and the Council on Environmental Quality. The U.S. Coast Guard, through IMCO and its subsidiary activities, such as the Maritime Safety Committee and the newly established Marine Environment Protection Committee has effectively spearheaded this combined interagency effort. Since bulk ships, including tankers, are now part of the MarAd program since their inclusion by the 1970 Merchant Marine Act, MarAd has played an increasing role in supporting this effort and will continue to do so in the future.

The MarAd Standard Specifications for Cargo Ship Construction provide guidance for merchant ship designers preparing detailed ship specifications, especially for ships to be built with Government Construction Differential Subsidy. First prepared in 1965, the Standard Specifications were updated in 1972. Currently the Agency is preparing a totally new Standard Specification for tankers. As a result of the increased emphasis placed on measures to control ship generated pollution, Section 70 - "Pollution Abatement Systems and Equipment" of the Standard Specifications was revised in its entirety in March 1971, to consolidate all pollution abatement features of cargo and tanker construction and operation to control oil, sewage and air pollution. Until recently, Section 70 has been advisory in nature. However, as a result of action taken by the Maritime Subsidy Board in August 1973 (Docket A-75), Section 70 is now a mandatory requirement for all tankers built under the MarAd Program. Section 70 is currently under review to ascertain if any new requirements are needed. The provisions of the 1973 Marine Pollution Convention, for example, are being carefully studied to determine what changes to Section 70 will be required to meet that Convention. As part of this review, we have noted certain difficulties and this brings us back to my previous point that two provisions, one a construction standard and one an operational discharge standard, will be difficult to achieve. These are the operational discharge standard dealing with oil content meters and oily water separators and the construction standard for segregated ballast.

Oil Content Meters and Oily Water Separators

Marine operations make up about 49% of the known total estimated annual oil pollution of the oceans. By marine operations I mean the movement of tankers, tank barges and other vessels. Not included in this are offshore drilling operations or other non-marine transportation operations such as refineries and petrochemical plants, industrial machinery and highway motor vehicles which make up the remainder of the known oil pollution. The known total for all the above does not include oil contributed by recreational boats, hydrocarbon fallout and natural seepage which, by some estimates, is as large as the known pollution. In all, this would make the marine operations contribution smaller proportionately but by no means insignificant. Quite the contrary; marine operations accounted for an estimated total of 2.3 million metric tons of oil pollution worldwide in the year 1970. More than half of this is from tankers. Almost a million tons are from all other vessels and the remainder is from tank barges. The known causes of pollution are usually characterized as intentional and accidental. Accidental causes include collisions, groundings, rammings, breakdowns, fires, explosions and structural failures. The term "intentional" gives an unfortunate connotation, but basically includes causes such as those resulting principally from vessel operating practices. These are tank deballasting, tank cleaning, bilge pumping, terminal operations and bunkering spills. Operational discharge accounts for more pollution than does accidental by a ratio of more than 4 to 1, although most of the spectacular publicity on pollution from vessels results from the latter.

While these figures are large, they would be much larger had not tanker operators taken voluntary measures, beginning in the early 1960's, to minimize dumping of oil to the sea. This was accomplished by adopting the procedure known as Load-on-Top (LOT).

Tankers designed without exclusive segregated ballast tanks will normally take sufficient sea water in their cargo tanks after discharging the cargo to insure proper propeller immersion and to provide good handling and sea-keeping characteristics and to maintain the required stability conditions. The ballast water that is put directly into the empty cargo tanks after the cargo is discharged comes into contact and mixes with the oil that adhered to the tank surfaces or remained at the suction mouths and cargo piping system after cargo discharge. This oily ballast must be disposed of in some way prior to arrival at the loading port, or retained on board and discharged to a shore reception facility. When the oily ballast is disposed of at sea, the empty cargo tanks are then filled with sea water which can be disposed of into the harbor at the oil terminal loading port.

This type of ballast handling operation, commonly referred to as "uncontrolled ballast discharge," causes all of the oil residue in the tank washings and approximately 15% of the oil residue from the tanks which were initially ballasted to be pumped overboard. The amount of oil discharged to the sea depends on the amount of oil that remains in the tanks after discharge at the unloading port. This is referred to as "clingage," and is considered to average 0.3% of the cargo capacity for crude oil and 0.08% for light oils.

Recognizing that the intentional pollution resulting from the uncontrolled discharge to the sea of the oily ballast water and tank washings represented a major source of ship-related oil discharges, the oil companies instituted the LOT ballasting procedure. On tankers using this procedure, the oil in the dirty ballast and tank washings is not pumped directly overboard but instead is retained on board and diverted to a slop tank.

When employing the LOT method, tankers on their return ballast voyage take on sea water in several of the cargo tanks in sufficient quantity to maintain required stability conditions, while the remaining empty cargo tanks are cleaned by butterworthing or similar tank cleaning process. All the tank washings are then pumped out of the cleaned tanks and transferred to the slop tank. After the tank cleaning is completed, fresh sea water is pumped into the washed tanks, which now contain clean ballast water. At the same time, the oily sea water in the cargo tanks which were used for ballasting is permitted to stand until the oil residue in the tanks has gravitated to the top. The decanted water in these tanks is now discharged overboard until the oil/water interface is reached. The oily slops from the dirty ballast tanks are then pumped to the slop tanks. At this point, the oil in the slops is given time to separate from the water by gravitating to the top. The decanted water under the oil in the slop tank is carefully pumped into the sea.

Upon arrival at the loading port, the clean ballast water is discharged and only oil in the slop tank remains. The new cargo is then taken on board, and is loaded "on top" of the remaining oil in the slop tank. The effectiveness of LOT depends on the length of voyage, type of oil, and weather, all of which affect the settling out and gravitating of the oil. In addition, effectiveness relates to crew training and skill in the operation. The practice of employing LOT has reduced this source of pollution by 90%. The result has been the elimination of over 3,000,000 tons of oil pollution per year. It is significant to note that this saving alone, which was accomplished voluntarily, exceeds the present total known oil pollution from all marine operations.

To further improve LOT, work must be done to improve oil/water separators, interface detectors and oil content meters. The 1973 Convention requires that all tankers be fitted with an approved oil discharge monitoring and control system. For enforcement purposes, this system must be provided with a recording device to produce a continuous record of the discharge in liters per nautical mile and total quantity discharged or of the oil content and rate of discharge. It must come into operation when there is any discharge of effluent into the sea and ensure that any discharge of oily mixture is stopped automatically when the instantaneous rate of discharge of oil exceeds that permitted by the Convention. In this connection, it might be pointed out that for 30 inch lines such as those used in very large tankers, a so-called quick acting valve requires as much as one to two minutes to close in order not to burst pipes nor damage valves or pumps. Tankers must also be provided with effective detectors for a rapid and accurate determination of the oil-water interface in slop tanks. The fact is that equipment to meet the Convention's standards exceeds today's state of the art for that equipment. With regard to oily water separators low flow separators (50-100 gpm) needed for cargo systems are not workable. In the case of oil content meters, the meter has to be recalibrated when different types of oils flow through the meter and the error of the equipment generally exceeds the 15 ppm accuracy required.

Installation of monitoring systems is required in existing tankers three years after entry into force of the Convention and in new tankers, upon entry into force. This provision permits time for development of monitoring devices suitable for the various grades of oil and for orderly retrofitting of existing tankers. Since the 1973 Convention applies to all grades of oil, persistent and non-persistent, i.e., crude oil and light refined, the Convention permits each Administration to waive compliance of the requirement for monitoring of light refined products until such time as this equipment is available. The Convention prescribes that IMCO will annually review the availability of such equipment.

While it can be expected that industry will initiate or accelerate development work to meet these requirements in new equipments, the Maritime Administration is undertaking an extensive R&D program to assist.

At the National Maritime Research Center (NMRC) in Galveston, Texas, designs are underway for an Oil/Water Separator Test Loop which will greatly increase the progress on the testing of oily water separation systems interface detectors; oil content meters, and related hardware for handling bilge and ballast waste, tank cleaning wastes, and waste from LOT procedures. The Test Loop will not only allow the testing and evaluation of oil/water separators but also will provide better control of testing parameters. Upon completion of the Test Loop, NMRC-Galveston will act as a certification agency for the Maritime Administration for oil/water separator systems.

To improve LOT effectiveness, MarAd has already obtained concentration profiles for dirty ballast, clean ballast, and slop tanks for several different crude oils. The profiles were correlated with settling time, oil density, and washing time for clean ballast. The data has been analyzed and is being applied to determine optimum ballast handling procedures and any additional treatment requirements.

Developed data indicates that separation of oil/water mixtures within slop tanks contain high concentrations of oil. In this area, different design concepts are being investigated for slop tanks and their internal structures to improve their use as gravity separators. In addition to basic tank geometry, vortex emulsion breakers, baffles, inlet and outlet configurations, and transfer procedures are being studied.

Therefore with the impetus that the 1973 Convention has provided, it is hoped that industry's efforts, augmented by an effective MarAd R&D program will overcome the current technological inability to meet this provision of the 1973 Convention.

Segregated Ballast

The 1973 Convention makes mandatory, in all new tankers of over 70,000 tons deadweight, contracted for on or after January 1, 1976, or delivered on or after January 1, 1980, the requirement that they be fitted with segregated ballast tanks sufficient in capacity to provide adequate operating draft without the need to carry ballast water in cargo tanks. During the ballast voyage, in any ballast condition, including the condition of light ship plus segregated ballast only, which condition excludes stores or fuel as part of the ship weight, the ship's draft and trim must meet the following requirements:

(a) Draft (amidship) = 2.0 + 0.02L, in meters.
(b) The trim by the stern not to exceed 0.015L.
(c) The draft at the after perpendicular must be sufficient to obtain full immersion of the propeller(s).

Ballast water may only be carried in oil tanks in weather conditions so severe that, in the opinion of the master, it is essential for the safety of the ship to carry additional ballast water in oil tanks. This additional ballast water must be processed and discharged in accordnace with the operational discharge requirements of the Convention.

This segregated ballast requirement is not technologically difficult to achieve. Rather, its difficulty lies in the fact that it will have an economic impact on tanker design, construction and operation because it will require the utilization of large dead, volumes which cannot assist in the earning capacity of the ship. In this connection it should be noted that world order books show a large backlog of orders for new tankers to be delivered prior to 1980. This backlog almost equals the world's present operational tanker deadweight capacity. In addition there are still almost two years to contract for additional tanker tonnage which could be delivered before the end of the decade. Therefore tanker tonnage exempt from the segregated ballast requirement will be sufficient to handle much of the world's crude oil transportation needs at least through the 1980's and well into the 1990's.

Still, because this requirement has such economic consequences and because the adoption of the requirement preceded the present world concern for energy, it is important to assure that its impact is mitigated to the maximum practical degree before that point in time when it does become a controlling design requirement.

The impact of this provision on the designs currently under construction in the MarAd Tanker Construction Program was investigated. It shows that the current National Steel and Shipbuilding Company's tankers of 89,700 DWT would lose 6,950 tons of cargo deadweight, (7.7%). The Seatrain Corp. tanker of 225,000 DWT would lose 14,700 tons of cargo deadweight (6.5%). The Bethlehem Shipbuilding Co. tanker of 265,000 DWT would lose 25,400 tons of cargo deadweight (9.6%). This amount of lost carrying and earning capacity is a price that will have to be paid to meet the current requirements. New designs specifically aimed at optimizing this requirement could not appreciably improve these figures either.

The level of segregated ballast that was adopted by the 1973 Convention was the result of a compromise of differing views. Maritime Administration studies to date indicate that the minimum levels of ballast required for safe, inballast operation, are significantly lower than the present 1973 Convention requirements. Since ships have taken on more ballast than is generally considered necessary because there was no penalty associated with doing so, ships have really not had operational experience of any significant amount in the lighter displacement conditions.

Model tests sponsored by MarAd at Stevens Institute and subsequent computer analyses resulted in minimum levels of ballast that are significantly lower than the IMCO requirements. The Oil Companies International Marine Forum (OCIMF) also demonstrated with full scale test voyages that the present levels of ballasting can be safely reduced by a large percentage. The Netherland's model work and Norwegian study of current practice also point to the possibility of acceptable levels lower than the current formulation.

The recent increase in bunker prices could have a significant effect on discouraging overballasting as well, in that operators are looking to reduce resistance and save fuel. The realization of the high costs of segregated ballast could also result in a concentrated worldwide effort at reducing the average levels of ballasted displacement. All of these factors point to potential future reductions in ballasting levels and the need for international effort at promoting a uniform reduction in these ballast levels.

MarAd therefore has proposed to IMCO, through appropriate channels, that a research program with the following goals and elements be pursued:

(a) Identify immediate improvements needed in the IMCO segregated ballast formulation in view of present designs and ballasting practices.

    1. Investigate impact of present formulation on current designs.
    2. Survey present ballasting practice of different bulk operators on 1,000 DWT to 500,000 DWT vessels.

(b) Determine minimum levels of ballast necessary for safe ship operations.

    1. Conduct analytic and experimental studies of structural response, comfort and other limiting considerations resulting from lightly ballasted conditions.
    2. Obtain full scale test voyage statistics at lower levels of ballast reviewing damages, repairs, crew comfort, time saved, fuel saved, etc.
    3. Conduct careful full scale correlation runs with two differently sized tankers (90,000 DWT and 250,000 DWT) measuring pitch, slamming, propeller racing and deck wetness frequencies along with sea conditions and structural strains in the bow area.
    4. Correlate full scale runs with model tests and computer runs.
    5. Perform maneuvering studies to determine the difficulty of maneuvering in and at low ballasted displacements.
    6. Perform model testing and computer analyses to determine the lowest necessary ballasting levels for safe ship operation.

(c) Determine the incentives necessary to induce masters to take advantage of the ability to operate tankers safely at lower ballast drafts.

    1. Investigate training, change in policy and other factors necessary to encourage ship masters to operate with less ballast. Consider the potential savings resulting from higher costs and the added cost of segregated ballast features as a guide to limits on financial incentives.

This action is in full keeping with the spirit of the 1973 Convention inasmuch as Resolution 8 of the Convention recommends that "IMCO take appropriate action to consider these ballast draft requirements, . . . and to examine them with a view to determining whether any improvement is required . . ."

Conclusion

While the adoption of the 1973 Convention was a truly significant step in raising pollution standards, it should not be considered the final solution to the prevention of global marine pollution. Because of the rapid amendment procedures of the new Convention permitting changes in the regulations as a result of developments or new technology such as the data developed at this Symposium and Workshop, international pollution standards will continue to be updated. This process should also be materially improved as a result of the establishment of the new Marine Environmental Protection Committee under IMCO. In addition, there is much to be done to assure that this Convention comes into force. There is also much to be done to upgrade our capabilities in the area of detection and enforcement to assure that the provisions of the Convention when they do come in force, are not hollow expressions of good intentions only. Nor should those provisions be unnecessarily onerous out of doubt or ignorance that they create distrust and abuse. There is still much to be done.

Scientific exploration must be continued and the fruits of that effort must be engineered into practical achievement. MarAd is firmly committed to the policy that strong and effective pollution control regulations can go a long way toward protecting the marine environment. However, before rigid standards can be established, we believe a definitive basis must be developed which indicates the need for such standards. This is particularly true when high pollution control standards require costly and sometimes unrealistic construction and design requirements for vessels. The work you have done and hopefully will continue to do can help a great deal in establishing the proper standards. I hope I've given you a little insight into some of the ship problems so that you will be encouraged to continue to work in your fields toward our mutual goals.

Regulatory Functions

Mr. T. A. Wastler
Chief, Marine Protection Branch
U. S. Environmental Protection Agency

Regulatory programs in marine environment usually exist either to prevent over-exploitation of a commercial resource or to protect a part of the environment from damage or destruction. International agreements for the protection of some specific types of marine resources have existed in one form or another for a number of years and recently, more general agreements directed toward protection of the general marine environment have been agreed to or are approaching agreement.

The International Ocean Dumping Convention was ratified by the United States on April 29, 1974. This country was the 6th nation to ratify the Convention which comes into force when 15 nations have ratified it. This Convention regulates the dumping of waste materials into the ocean from barges and other floating craft. Several highly toxic bio-accumulative or otherwise damaging waste constituents or materials are prohibited as other than trace contaminants. Mercury and its compounds, cadmium and its compounds, organo-halogens and oils and greases are such materials. Other waste materials may be dumped under permit by the nation from which they are transported. You have heard about the provisions of the IMCO Convention which is in the final stages of approval. This Convention, as was mentioned, deals with the operating discharges from ships such as tank cleaning and cargo related dumping or discharges. In addition to these Conventions, negotiations are beginning to establish an international basis for the regulation of deep sea mineral resources and for regulation of land based sources of pollution.

No international convention for the regulation of the environment can be effective without an active and efficient program to monitor the environment in terms of what is being regulated and what effects are being controlled. The marine environment, particularly the open oceans, has been primarily the working place of the research community; and the development of an integrated monitoring program to serve regulatory needs is just beginning. The IGOSS project on Marine Pollution Monitoring is a major step in that direction.

In discussing how regulatory programs need and can use monitoring data, I would like to cover three general topics: First, the kind of information needed for regulatory purposes; second, the present situation with regard to the availability of such information; and, third, the types of developments we would like to see started.

The first question is - what kind of information do we actually need for the implementation of an adequate regulatory program? Whether the source of the pollutants is from outfalls, from direct ocean dumping, or from the operating discharges from vessels, the type of information needed from the environment itself can be grouped into four categories:

1) We need to know what materials are being discharged and are likely to be discharged into the ocean. This, of course, is not the type of

information that is acquired in a marine monitoring program itself, but it is essential to have such information in order to know what observations should be made on the marine environment. From a knowledge of the types and distributions of waste sources, the sampling requirements for marine monitoring programs can then be developed.

2) From a knowledge of waste types and sources, the locations of probable impact from these sources in the ocean, particularly in the near shore areas, can be developed and the appropriate parameters to identify specific pollutants and their impacts can be incorporated into a marine monitoring program.

3) From a regulatory standpoint, in terms of monitoring the oceanic environment, those parameters of importance would be persistent synthetic or natural organic materials not normally found in the ocean, and trace materials, particularly metals of a toxic and bio-accumulative nature. The impacts of these materials would be very difficult to characterize from a monitoring standpoint since they would probably appear as changes in the viability or appearance or non-appearance of various forms of life in certain areas. A monitoring program to characterize these types of impacts probably would have to consist of broad scale biological surveys in certain geographic areas rather than monitoring at point locations. Information is needed also on water movement and circulation so that the probable areas of impact of various forms of waste can be traced from their sources.

4) An effective system for collecting and disseminating these types of information is required together with a mechanism for identifying adverse trends before critical or irreversible conditions are reached.

The next point I wish to mention is where we are now in terms of monitoring needed to support regulatory activities. This can be summarized very briefly by simply stating that we do not have any oceanic monitoring program effective enough to support a regulatory function. The ratification of the Ocean Dumping Convention by each signatory nation will require a commitment by that nation to conduct monitoring activities to determine the effects of waste dumped under the permits that it issues. Actual monitoring efforts so far are minimal. In the United States, we do not yet have an effective ocean monitoring program, although we anticipate that such a program will be initiated during this calendar year. Even then, however, our ability to anticipate and determine effects is extremely limited. In terms of oil and petroleum derivatives in general, which are the primary concern of this symposium, our basic regulation and criterion as to a trace amount is that quantity which will make a visible sheen on the surface. This approach may be useful in determining the impact of sewage sludges and industrial wastes dumped from barges or out-falls, but it does not lend itself to control of materials such as tar balls and floating films which may be observed on the surface of the ocean, but for which no visible source of pollution can be found. What then would we like to see in the way of development in marine monitoring from the standpoint of the regulatory program? First, we need a development in technology and technique which would permit us to measure on an automatic and remote basis the concentration and distribution of floating materials, such as tar balls and films on the ocean. Second, we would like to see analytical development in the analysis of such materials so that it would be possible to trace them back to their sources. Third, we would like to see the establishment of key biological or chemical parameters which should give us an idea of the health of the various parts of the ocean before critical conditions are reached. Fourth, we would like to see the development of a mechanism for the rapid collection and dissemination of this information to the appropriate international and national regulatory organizations.

In summary, I would like to point out that the development of international agreements and conventions for the control of marine pollution are useless without the parallel development of the mechanisms and technology for the technical implementation of these agreements. When we talk about international agreement to control marine pollution, it must be in the context of what kinds of scientific and technical programs are required to carry out the spirit and intent of the convention. In the case of the pollution of the world's oceans, we must think clearly in terms of what we need to know about that ocean on a regular basis and make sure that whatever monitoring programs are developed and implemented are done with full knowledge of the regulatory commitments of the various nations in mind and the technical requirements for meeting these commitments.

Regulatory Functions as Related to Vessel Construction and Operation

Captain S. A. Wallace
Chief, Marine Environment Protection Division
United States Coast Guard

I am here today representing Rear Admiral Benkert, the Chief of the Marine Environment and Systems of the United States Coast Guard. He had a schedule conflict which did not permit him to speak to you as planned. He particularly likes to speak to scientists, so I know he regrets not being here. In examining the list of attendees, one or two things occurred to me that may raise questions. If we have time for questions, I will be glad to answer at the conclusion of my talk.

I serve as U. S. Chairman of the Marine Pollution from Shipping Working Group under the bilateral agreement between the United States and the Soviet Union for protection of the environment. In the Soviet Union, this Group is under the auspices of the Ministry of Merchant Marine.

I am the scientific leader of the Working Group on Marine Pollution pursuant to the U. S.-France bilateral agreement on oceanography. I do have a program colleague in the room, Jean Claude Mourlon, who is from CNEXO in Paris.

I had been deeply involved in the 1973 Marine Pollution Conference of which so much has been said today, participating in four preparatory sessions in the conference itself and in the Marine Environment Protection Committee which was newly formed in IMCO after the Conference; and I did serve as the U. S. spokesman at the Conference in Committee 2, which was responsible, among other things, for developing Annex I which governs oil. This Convention is the product of our many months of labor, and I am prepared to refer to it if anyone has a question. I had a colleague on the U. S. side who is present today: Captain George Steinman of MARAD.

Now the application of monitoring, in the sense that you are using the word in this symposium, is in its very early stages of evolution in serving the needs of regulatory programs in the United States. We do have research and development efforts underway. We audit the development of effective monitoring in related fields, but we have yet to apply monitoring to any significant degree in our regulatory programs.

I am going to discuss briefly our legal mandates and I ask that you view these mandates as constituting discrete functions, many of which lend themselves to monitoring applications, and for the benefit of our colleagues from other countries, I must say that, after examining the regulatory schemes effective in those countries, our system here in the United States is analogous. We have statutes; we have agencies responsible for implementing those statutes; and most of these agencies publish regulations. The Federal Water Pollution Control Act, Section 311, which has aptly been termed an act within an act, is our chief mandate; that is, the Coast Guard's chief mandate, in oil and hazardous substances pollution abatement. Under that section of the Act, we are responsible for transportation-related facilities. The EPA has responsibility for regulating non-transportation-related facilities. The Coast Guard has issued its regulations for vessels and for terminals; these regulations will be effective the first of July 1974. We are presently, together with other agencies in the U. S. Department of Transportation, developing regulations for transportation-related facilities in other modes of transportation--rail, highway, etc. There is a $5,000 civil penalty for violation of these regulations and the agency that promulgates the particular regulation is responsible for assessing the penalty.

With regard to the occurrence of discharges, the Coast Guard is designated as the appropriate agency for notification, a function which, through regulation, we now share with EPA. Failure to notify by the person in charge of the vessel or facility responsible for a spill will make that person subject to a $10,000 criminal fine or one year in jail or both. The discharge makes the discharges subject to a "no-fault" penalty. The polluter, if it can be established through substantial proof, is subject to up to $5,000 in civil penalty. This program is administered by the Coast Guard, either through our own investigations, through EPA's investigations, or through investigations by any of the 50 states.

We have a function we call "response", which is synonymous with clean-up. The Coast Guard is responsible for response to spills in coastal waters, the Great Lakes, harbors, estuaries, etc. The EPA has the inland area. We work with them in developing contingency plans.

The Coast Guard manages a pollution fund that is used to finance the clean-up of spills where the polluter either fails to do so, or does not do so properly in the opinion of the Federal official on the scene.

We maintain a National Strike Force, composed of three teams, Atlantic, Gulf, and Pacific, located on those coasts. These are highly trained, well-equipped teams, with quick air transportation at their disposal, who are dedicated to responding to spills and available to anyone who needs them, not just the Coast Guard. This is a national strike force. If the EPA calls for them, they respond immediately, just as they would to a Coast Guard District Commander. The Coast Guard also maintains a national response center on behalf of several agencies which make up what is called the National Response Team. This team is responsible for planning on a national level for developing the procedures to be followed when spills occur. Also, this team can be convened in the case of a major spill with severe ecological or political ramifications.

Now, in my view, we need monitoring in the response area to serve several purposes: To help us detect spills; to establish the dimensions of the spill; to assess when our clean-up is effective; and to serve as evidence in enforcement proceedings against the polluter.

The Ports and Waterways Safety Act was mentioned earlier; the Ocean Dumping Act, and the Marine Protection Research and Sanctuaries Act have also been discussed. The Coast Guard has several roles here. Essentially, we enforce the permits issued by EPA or the Corps of Engineers, depending on what substance is to be dumped. We ensure that dumping is carried out in accordance with the permit. We have a surveillance and monitoring (in the non-scientific sense) role in this. We do have authority to issue regulations. However, we do not intend to do so unless a clear need arises. A pattern of permits presently exists which makes regulation-making on our part unnecessary. With respect to research and monitoring, we will be working with NOAA and EPA in assessing effects of dumping.

The Oil Pollution Act of 1961 in the United States implements the 1954 Oil Pollution Convention. We have said much about the 1973 Convention. We have expended a great deal of effort, blood, sweat, and tears toward developing that Convention, but what we have today internationally is the 1954 Convention. Generally, this prohibits discharges within prohibited zones around continental land masses--this means within 50 to 100 miles of land depending on what land mass we are speaking of. It establishes a specific oil content for water discharge by tanker or other vessel operations to 100 ppm, and requires an oil record book be kept by each tanker. I might emphasize that this Convention applies only to oil and only to a portion of the family of oils--the so-called persistent oils or black oils. There are two sets of amendments worthy of note: The 1969 amendments to the 1954 Convention and the 1971 amendments. The 1971 amendment establishes tank size limitations. The 1969 amendments generally prohibit discharges within 50 miles of land; state that the discharge may not exceed 1/15000th of the cargo capacity of the tanker (or 100 ppm for other vessels); and state that the instantaneous rate of discharge shall be less than 60 liters per mile with the tanker underway. We do not know when these amendments will come into force. Some 18 nations have ratified the 1969 amendments, including the United States, and some 28 are required to ratify to bring the amendments into force. It is, I suppose, conceivable that the 1973 Convention will come into force before the 1969 amendments. I will answer questions about the 1973 Convention if there are any questions stemming either from my discussion or those preceding.

With regard to the use of monitoring data to assist with regulatory function, the Coast Guard does not consider itself a primary user of raw data, and perhaps "raw data" is a poor term to use in this scientific forum, but please blame the ignorance of the layman. The Coast Guard will and does assist other agencies who have a responsibility in this area in gathering data. We feel strongly that ultimately, the data must be used to determine the efficiency of the national program. We are engaged in research and development efforts to improve our detection capability. We have in operation sensor-equipped aircraft with what we call off-the-shelf sensors--ultra-violet and infrared--and we are developing a much more sophisticated system for future use although we cannot determine that it will be practical and cost-effective until we put it into operation. We are also considering on-site sensors in busy harbors and sea lanes which we would hope can help us detect violations of our environmental standards.

Monitoring for a regulatory purpose through scientific means and procedures is a procedure which is yet to be exploited in our regulatory operations. We are certainly open to suggestions and recommendations and, to the extent that monitoring programs mean money, we are open to persuasive arguments related to cost-effectiveness, and budget justification, one of those nasty things that we are up against at least once a year. Ultimately, we will need scientific means to determine whether our regulatory efforts are bearing fruit--which means cleaner water--and where our efforts are shown to be ineffective, we will need these means to determine how these regulatory efforts can be reshaped to meet the mandate of national pollution policy. Mr. Stansby remarked that monitoring is not an end in itself; neither are regulations. Our goal is effective protection of the marine environment for the ultimate good of mankind. We will do the regulating and, given the tools, we will do the monitoring to achieve this goal.

DISCUSSION

Question: Do we have specifications for detergents used for responding to oil spills?

Wallace: It is the policy of the United States--through the responsible agency which in this instance is EPA--that we not use chemicals except in a very limited way in combatting oil spills. There are several approved herding agents we may use. We do not use sinking agents. We do not use any agents that will apread the oil or disperse it into the water except in an emergency. An on-scene coordinator does have the authority, where safety of life and property is involved, to use dispersing agents. But, as a rule, such use is not allowed in the United States. I realize that many other countries feel differently. We do have a considerable amount of information about this, and our research and development is continuing with the hope that we will be able to show that such agents can be used without harming the environment. Some chemicals are more harmful to the environment--and I am stating this, not as an expert, but according to EPA--than is the oil which they would disperse. If I can provide you with any useful information on these chemicals, I will be happy to do so.

Question: Is it reasonable to have international standards for pollution control in view of the lack of international standards for measurement? (Questione referred to a previous paper submitted by Mr. Richard Morse, NOAA)

Wallace: Well, I cannot speak for Mr. Morse. I would think though, that he was speaking of scientific measurements, perhaps finely calibrated measurements, which can be proven in a laboratory. I think that at the 1973 Marine Pollution Conference (which incidentally was an international conference, not an "IMCO" Conference) the point was made that this is a fine, but important distinction. At that conference, at least so far as the technical standards and regulations are concerned, these points were developed by people who knew the sea and ships. I am not talking about what went on in Committee I and the articles that had to do with international law in its broader reaches, but to technical standards. And we believe this is an entirely defensible position which can be shown, which can be demonstrated, which can be measured. And here I would disagree with one previous speaker with regard to the state-of-the-art. With very little stretching, current techniques are adequate, if not today, at the very least by 1976, which as you probably are aware is the date which fixes the rules for new ships. I think we are probably talking about two different kinds of standards. I would certainly yield to Dick Morse, but I know what kind of standards we were talking about in Conference Committees, and while we did apply a great amount of scientific work particularly with bulk chemicals, we used tried and true time-tested nautical measures of oil when we dealt with the Annex I. I do not personally believe there is an anomaly here.

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The following telegram sent by Dr. N. J. Campbell, Chairman of the Working Committee for IGOSS, was read. Dr. Campbell was unable to attend because of health reasons.

> "Sincerely regret my inability to attend and participate in the deliberations of your Symposium and Workshop; however, I would like to express my best wishes for success to all those countries and participants taking part. Much depends on the outcome of your decisions and work which will have far reaching effects on setting the future stage for marine pollution monitoring research and investigations by the IOC. I am certain your approach to these problems will be followed in many other fora since it cannot help but be judged as a breakthrough in the progress and development of such work, and in the capability of IGOSS to respond to the needs of such things as the Stockholm Resolutions and of Member States of the IOC. We will all be looking forward to launching the Pilot Project on Marine Pollution Monitoring as soon as possible. Best wishes and good success."
>
> N. J. Campbell, Chairman W/C IGOSS

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Concluding Remarks

Dr. Thomas S. Austin
Director, Environmental Data Service, NOAA

When the Chairman asked me if I would give the so-called "wrap-up," I indicated that I would be happy to speak on the philosophy and concepts of data management. He very tactfully suggested that the wrap-up does not concern concepts of data management, it concerns what we hope the workshop will achieve in the next few days. It's a little like the scientist who had worked for long years on earthworms and as he was standing in for his orals the first question was, "Mr. Doe, would you discuss elephants." So he thought for a moment because he didn't know anything about elephants and he said, "Well, the elephant is an animal with a trunk and a tail and the tail is round like an earthworm. Now you take earthworms and . . ." So that's what I propose to do. I'm going to discuss the elephant and then I'm going to ease into earthworms before I'm through.

I think this is most interesting and appropriate because I think it's a major step forward--the Pilot Project which will lead to, I'm sure, a much more viable and global concept. One only has to remember that approximately 100 years from last year, the Challenger embarked on the first of the major round-the-world oceanographic cruises. To many of you, the name Challenger, subsequently coupled with names like the Meteor, Lomanosov, Atlantis, Discovery, Umitaki Maru, Jean Charcot--the list goes on and on--highlights the fact that studies of the oceans on a global basis are truly of international concern. As a result of exploration and description, they are now beginning to analyze mechanisms and rates of change, and this all leads to learning to predict. Now, certainly the processes that have been identified are many. The thermal characteristics of the ocean--I have a note here, apologies to the interpreters if I describe it as the internal thermal commotion in the ocean--the chemical balance or imbalance which is one of the aspects that you have addressed yourselves to the past 3 days and will address yourselves to in even greater detail the rest of the week and early next week. Surface and subsurface interactions of the sinking at the Poles, the return through upwelling, and circulation on macro, meso, and micro scales.

Now, what we have been doing--we, collectively as oceanographers of nations--is establishing baselines, probably motivated by the innate curiosity of man and the desire to learn the relationships between ocean phenomena and weather, transportation, food, and recreation.

Certainly we have come to realize that no one nation has the resources to do the task that must be done. No one nation would have the resources to adequately, particularly in a synoptic concept, look at the North Atlantic or the North Pacific, South Atlantic, South Pacific, or Indian Ocean. There must be international cooperation--nations working together. The examples are many and I shall not dwell on them now, but the Intergovernmental Oceanographic Commission, which has now had about 1 decade of life, had its conception to bring together the scientists of the nations of the world that were interested and are interested in the oceans.

IGOSS was the first of the major surface service aspects of the IOC. The first project was the BATHY Pilot Project, which was a multination effort to bring together with the cooperation of meteorological organizations and communications capabilities information primarily through the use of the Bathythermograph, that would permit biweekly analyses of the temperature conditions in the North Atlantic. The pilot project was a success, and certainly it is hoped that many other nations than those in the pilot project will become involved in this concept.

Man's activities have led to recognizable and, as you have learned during the past 3 days, to a degree measurable impacts on his environment. I like to use the word "inadvertent" because I am confident, as a member of the generation that probably caused a lot of the recognizable and measurable changes to the environment, that these were inadvertent. Regrettably, it has not always been official. It certainly was the recognition of this that led the IGOSS System to the development of the concept for and the development of the marine pollution monitoring program. A decision was made carefully and intentionally that the first phase, the operational phase of the Pilot Project, would speak only to petroleum hydrocarbons. This particular form of a contaminant, a pollutant, was chosen because it seemed to hold out the greatest chance for success in terms of the objectives of the Pilot Project. It had a visual aspect--tar balls and oil slicks. You have heard a number of papers that suggest there have been significant analytical breakthroughs, advances, in the general area of chemistry of the hydrocarbons. It would allow monitoring pretty well on a global basis among areas where one may expect a reasonable high to low level of pollution. I hate to use the word high, but certainly comparatively speaking, the measurable levels should be related to those areas of the world's oceans where, hopefully and conceivably, there would be a much lower level.

If I may have the first slide. You have already seen this slide which will be used by the people in the workshop in terms of their first review of suggested areas for changes, if such are in order. The Symposium in the last 3 days has essentially laid the groundwork, exposed those who are going to be involved in the workshop to the relative levels of contemporary technology so that they make reasonably sound decisions as to what the pilot project should encompass. What is proposed is also under consideration within the United Nations Environment Program, the EARTHWATCH and the related Global Environmental Monitoring System--"an assessment of the state of the ocean pollution and its impact on marine ecosystems, and an improved international system allowing the monitoring of the factors necessary for the understanding and forecasting of disasters and implementation of an efficient warning system."

The EARTHWATCH speaks to a broad spectrum of environmental phenomena, certainly one of which is pollution from petroleum and petroleum products. The IGOSS Committee in its considerations and reports has recognized the value of the results from the Pilot Project as an input to UNEP and, in turn, UNEP has recognized the value, and I may stand corrected, but I believe is providing a modest level of support.

In the last 3 days, experts from all over the world have gathered here in this building to review the state-of-the-art in preparation for the workshop.

Now, what is the objective of the Pilot Project? Let me refresh your memory (although it probably is unnecessary)--to initiate and evolve an internationally coordinated program for marine pollution monitoring, initially in selected ocean areas. To a degree, the terms of reference indicate that the Workshop will be developing the details to provide an exchange of data and information among nations (probably very significant) and intercomparability of data for making assessments of the periodic state and degree of contamination of the marine environment. There must be a degree of standardization if we are going to compare the results obtained from the Pilot Project, as these results are from different ocean areas of the world.

The highlights of the review for the last 3 days spoke to sampling and analytical methods, standards and intercomparison criteria, oil in marine organisms and sediments, analytical techniques for each, as well as tar balls, particulates, and aromatic hydrocarbons.

Now what specifically is the workshop charged to do? With the results of the Symposium in mind, with the objectives of the Pilot Project always in front of them the workshop is charged to:

- Review and finalize the operational plan. Review and finalize means in part: review, assess, modify if needed, and finalize.

- Recommend studies and actions required for expansion and development of the Pilot Project. The Pilot Project, just as the term "pilot" implies, is the initial step in what IGOSS, IOC, and others involved, hope will become an on-going operational global concept.

- Define the recommended technical assistance programs and training and education projects. These to highlight the needs so that the scientists, particularly those in the developing countries, may receive the training needed so that they may become an integral part of the Pilot Project, and even more important, of the continuing nature of the monitoring program on down the road.

- Focus the R&D aspects, if you will, the technical aspects, to speak to the methodology, analytical standards, data handling, contents of the final report, what guides and manuals will be needed for those participating in the Pilot Project, recommendations as to whom should have the responsibility for the preparation of these guides, and in what manner the technical assistance programs will become involved.

Now, I spoke to the elephant, the trunk, and the worm. I was just going to say, let me turn to the worm, but I simply refuse to put the data management aspects of this in the category of a can of worms.

If I could have the next slide please. I am very interested in showing you a concept we have been working on, are developing somewhat as a national concept, and hope to broaden to an international concept of how environmental data should be managed. What this speaks to is that data management should start when the concept is developed. I am using it here at this time primarily because the project with which you have been concerned during the last 3 days and which the Workshop will continue to be concerned with seems to very neatly highlight this concept. Considerations concerning the handling of the data continue through the planning phases, which will really be the Workshop, on through the operational aspects. In other words, plans should be made for the manner in which the data that will be recorded on board the ships and in the labs will be handled. These data are being collected for a purpose. Therefore, every effort should be made to see that the data in their reasonably standardized forms as quickly as possible are in the hands of the users, the primary users. Then they should be made available to the centers, whether they happen to be the national centers, or the World Data Centers, or to a group such as ICES, the International Council for the Exploration of the Sea, so that these data may then have a wide dissemination to the secondary users. Whether the secondary users happen to be scientists, nations, or whoever may be interested.

So Mr. Chairman, I think the proper thing at this moment is to wish those that will be in the Workshop, Godspeed, and to extend the sincere appreciation of those involved to the participants during the last 3 days and particularly to all of you who have had the intestinal fortitude to sit here until this late hour without having a coffee break. Thank you very much.

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CONTRIBUTED PAPERS

TOPICAL SESSION I.

Sampling Methods and Techniques: Oil Slicks, Tar Balls, and Particulates

NBS Spec. Publ. 409, Marine Pollution Monitoring (Petroleum), Proceedings of a Symposium and Workshop held at NBS, Gaithersburg, Maryland, May 13-17, 1974 (Issued December 1974).

QUANTITATIVE MONITORING AND VARIABILITY OF PELAGIC TAR IN THE NORTH ATLANTIC

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St. George's West, Bermuda

Quantitative collection of pelagic tar (petroleum residues found on the surface of the open ocean) began in 1969 [1,2] and has been carried out in many parts of the world since then [3,4]; but few data are available to estimate the sampling error. The question which we address in this paper is: If a single sample is taken at a particular place at a particular time, how representative is this amount of tar of the amounts which would be collected by repeated sampling?

There are three types of data which can be used to answer this question. The first and most abundant type is the series of values obtained along a single cruise track. In most such published data stations (where neuston tows are of the order of 1 km in length) are usually hundreds of kilometers apart; and so from such a set of data one cannot tell whether the large variations observed reflect variations in the amount of tar on a scale of tens to hundreds of meters (e.g. Langmuir [5] windrows) or tens to hundreds of kilometers. The most closely spaced stations [6] show data with variability of a factor of 50 on a distance scale of 1 km. Needless to say, a single cruise track can tell nothing about time variation unless the track is repeated at a later date.

Thus the time series data we have obtained at Station S [7] (32°10'N, 64°30'W) near Bermuda, although meager, are uniquely valuable in assessing the variability of sampling by other investigators. This time series, taken biweekly since 1971, was augmented by a series of tows at approximately two-hour intervals in February and August 1972. The short-term series were intended to give information about the reliability of the samples in the long-term series. Full tables and details of method are given elsewhere [3].

Since variations occurred of more than a factor of 100 in the amount of tar collected, and variations of over a factor of 10^4 in the amount of Sargassum collected in the long time series, it seemed plausible to inquire whether the tar was in some way associated with Sargassum colonies, since such colonies collected by dip net often contain tar lumps. Figure 1 shows the correlation on a log-log plot. Although there is a slight correlation (R = 0.39) in that extremely high values for Sargassum do not occur together with extremely low values for tar, or vice versa, it would appear that substantial quantities of tar can occur without the presence of any Sargassum (as of course is observed in waters other than the Sargasso Sea), and that quite large ratios (250) of Sargassum to tar can also be observed. The ratio of arithmetic mean wet weights is 25 Sargassum to 1 tar (the ratio of geometric means is of the order of 10 to 1), corresponding to a line of slope unity drawn through the cluster of points.

The raw data of the two short-term time series are displayed in Figure 2. Note that even at intervals as short as an hour or two, variations in the amount of Sargassum and tar of a factor of ten or more are quite frequent, in spite of a deliberate attempt to average out any inhomogeneous distribution due to the Langmuir [5] circulation. For example, tows typically were made in a circle of approximately 1 km diameter. Depending on wind conditions, Langmuir windrows are spaced from 10 to 50 meters apart, and such a tow would have intersected 20 to 100 windrows at varying angles.

Correlation of Sargassum and Tar in these series (Fig. 3) followed the same pattern as the long time series, except that in February (S-356) the Sargassum/tar ratio was of the order of 150, and in the August series (S-365), this ratio was only about 2. Correlation was not significant: R=-.03 and +0.14 respectively.

As is clear from Figures 1 and 3, and as we have noted elsewhere [3,8], these values are more or less normally distributed on a logarithmic scale, and thus the geometric mean and the relative standard deviation (ratio to the geometric mean) are the relevant statistical parameters for describing a set of data. These parameters are displayed in Figure 4. Note first that the relative standard deviations of the tar values for S-356 and S-365 are essentially the same, although the average values differ by a factor of 10. On the other hand, the relative standard deviation of Sargassum in August (S-365) was much larger than in February (S-356). Furthermore, the standard deviation of the two short-term time series is only slightly smaller than for the two-year series of biweekly measurements. This implies that the additional variance resulting from long-term cycles is relatively small compared to the variance of sampling.

To investigate the long-term and short-term cyclic behavior of the tar and Sargassum data, a power spectral analysis of the time series was made [9,10]. Although the number of data points was really insufficient for any details of cyclic behavior to be elucidated, certain aspects of the time series were readily apparent from the results. Figure 5 shows the power of spectral estimates for Sargassum and tar each taken independently, and also the cross-spectrum amplitude. The annual cycle of Sargassum [11] shows up clearly as does a seven-week cycle. In the tar spectrum, the prominent feature is a cycle of approximately ten weeks duration. The cross-spectrum essentially follows the Sargassum but with less pronounced features. The occurrence of approximately two-month cycles for both Sargassum and tar lends some credence to the notion that this reflects meso-scale processes of ocean circulation with a relaxation time of approximately two months [12].

Spectral analysis of the short-term series shows no significant structure (Fig. 6) and the dependence of spectral estimates on frequency is characteristic of a Markov-like process with correlation becoming weaker as the time separation between stations becomes greater. For the best analysis of time series, data should be obtained at regular intervals without any omissions. No data presently available on pelagic tar satisfies this criterion rigorously, including our own.

In summary, the variability of sampling by neuston net for either pelagic tar or Sargassum is very high, and even the results of successive tows may differ by a factor of ten. The standard deviation is of the order of 0.5 log units, a factor of 3. The standard deviation of the geometric mean of ten to fifteen neuston tows may be estimated to be approximately 0.15 log units, or 40%. In other words, a single neuston tow is representative of the general area where the tow is made only within a factor of ten. In view of this, elaborate techniques for flow measurements [8] are unwarranted, and correction to dry weight or removal of non-petroleum materials, worthwhile only if the relative amount of these materials in the tar lumps is considered to be of intrinsic interest. The IOC-WMO recommendations [13] for analysis to determine dry weight thus involve a great deal of unnecessary labor and should be replaced by determination of a simple wet weight value.

Acknowledgements:

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Key Words: Petroleum, Tar, Sargassum, Sargasso Sea, North Atlantic, Neuston, Sampling, Analysis of tar.

This is Contribution No. 598 from the Bermuda Biological Station.

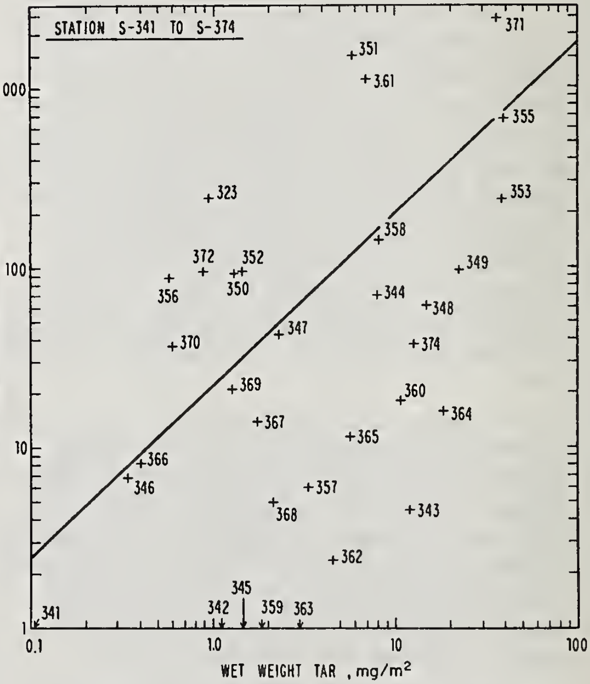

Figure 1. Correlation of wet weight of Sargassum and pelagic tar. The line corresponds to a 25:1 ratio.

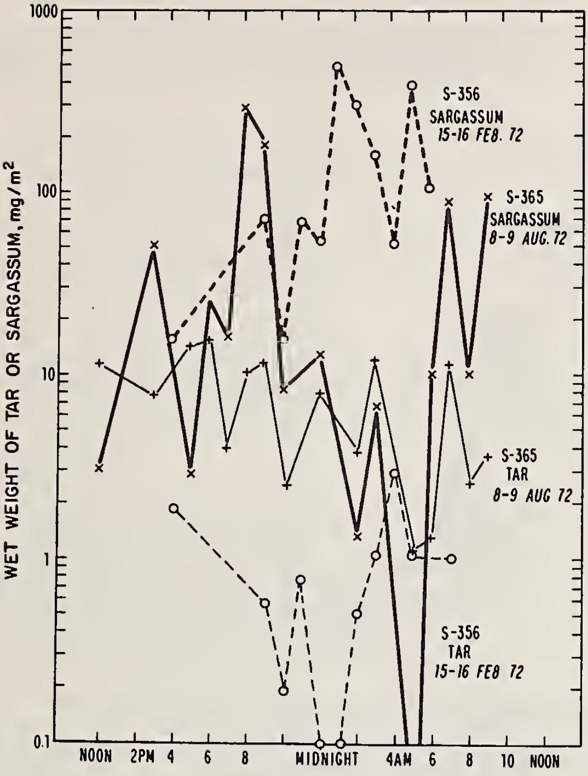

Figure 2. Short-term time series of Sargassum and tar obtained in February and August 1972, stations S-356 and S-365.

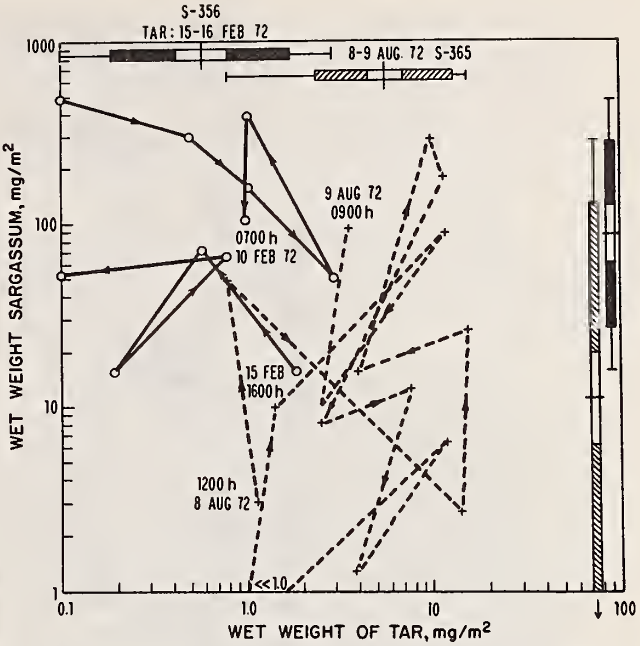

Figure 3. Correlation of Sargassum and tar: Data of Figure 3. Bars at top give statistics for tar, at the side give statistics for Sargassum. Central line is geometric mean, white bar is relative standard deviation of mean, dark bar is relative standard deviation of single datum, and extreme limits give the range.

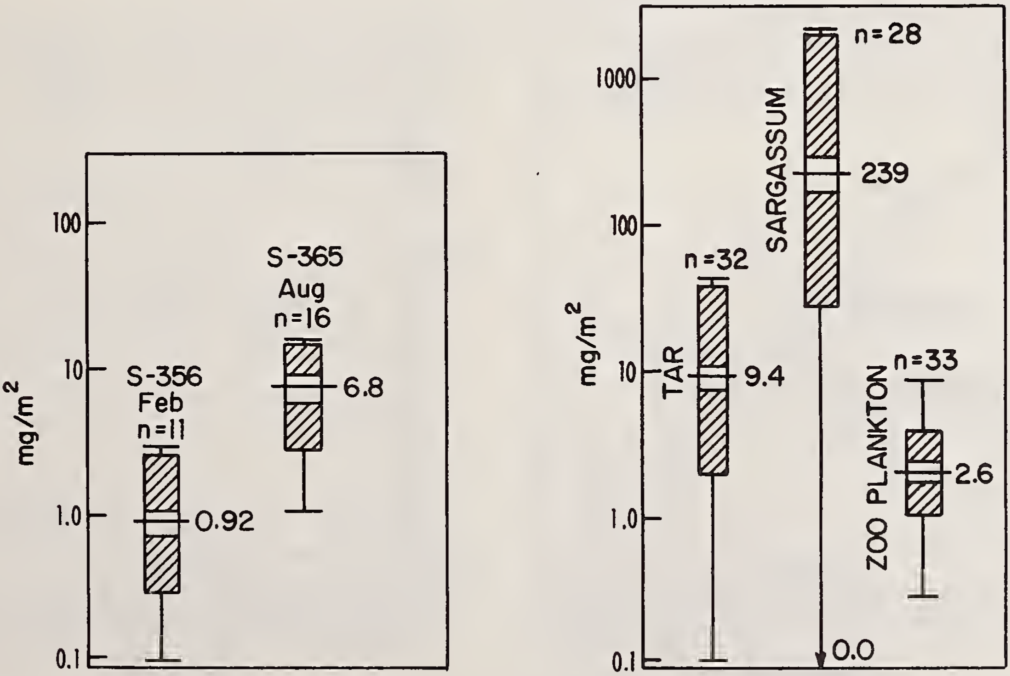

Figure 4. Comparison of short-term statistics (left) with long-term statistics (right). Bars express same data as Figure 3.

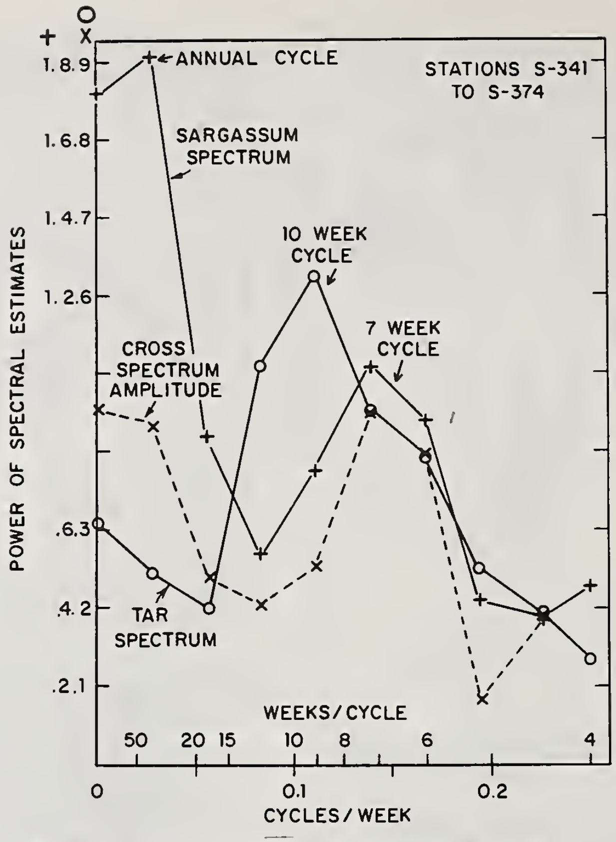

Figure 5. Spectral analysis of long-term time series.

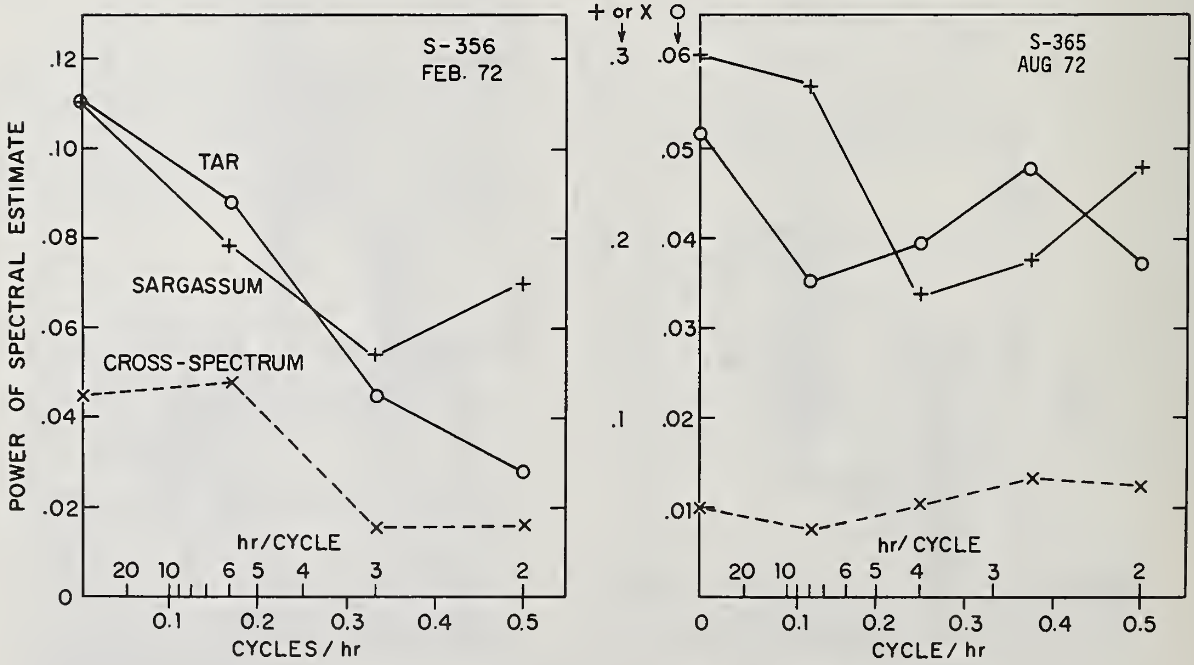

Figure 6. Spectral analysis of two short-term time series.

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TAR BALL LOADINGS ON GOLDEN BEACH, FLORIDA

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Disclaimer:

The contents of this report represent the findings and views of the author who is responsible for the facts and accuracy of the data presented. The paper does not necessarily reflect the official views or policy of the U. S. Coast Guard.

The sampling of beach tar from a sandy coast was performed for one year in order to evaluate the effect of sampling zones of varying sizes and the effect of tar build-up on the beach with time. In addition, the effect of wind on tar deposition was also determined.

The area selected for study is located within a uniform twelve mile tract of beach running nearly due north and south between Fort Lauderdale and Miami. The actual sampling site is located along a 1.4 mile stretch belonging to the town of Golden Beach. This area is reserved for use only by local residents, and is uninterrupted by bays, cuts, or breakwaters.

The area was divided into five zones: 20, 40, 80, 120, and 160 feet in width, with interzone spacings of 60, 120, 240, 300 feet, respectively. The zones ran consecutively from the smallest (20 ft.) zone situated furthest north to the largest (160 ft.) zone situated furthest south. The zones were staked out and cleared of all debris prior to sampling.

Usually all five zones were sampled each weekday (five days per week) over the entire period (September 1971 to September 1972). However, due to sporadic mechanical beach cleaning by bulldozer and occasional severe weather conditions some weekend sampling was performed in order to compensate for lost weekday coverage.

The actual tar pick-up involved non-replacement sampling and weighing of all solid and semi-solid pieces of tar/oil. Frequent surprise spot checks by an independent sampler rarely turned up more than ten percent additional tar/oil. All sampling was accomplished within 3-1/2 hours of low tide since almost all of the tar stranded at the high tide mark in a narrow zone 4-5 feet in width.

The presence of non-petroleum inclusions in the tar samples (shell, sand, water) inflated the weight of stranded tar so that the actual petroleum weight represents approximately 75 percent of the reported weights.

No extraneous fluctuations are evident in tar loading on the smallest (20 ft.) zone when compared to the largest (160 ft.) zone. Figure 1 presents total monthly weights of tar stranding in the 20, 40, and 160 foot zones. All data was normalized to 100 foot zones. Although the same general fluctuations are consistent for these zones, proportionately more tar is deposited in the smallest zones. However, this is not due to relative size differences between zones, but rather due to their relative positions on the beach within the tract area. Relative monthly fluctuations in tar loadings in each zone were compared using root-square differences. This was done after normalizing monthly totals from all zones to the total annual tar loading value in the 20 foot zone. Essentially this allowed comparisons of relative monthly fluctuations rather than absolute amounts. In this way the beach bias shown in Figure 1 was negated.

The root-mean square values are presented in Table 1 as percentages of the total annual 20 foot zone tar value.

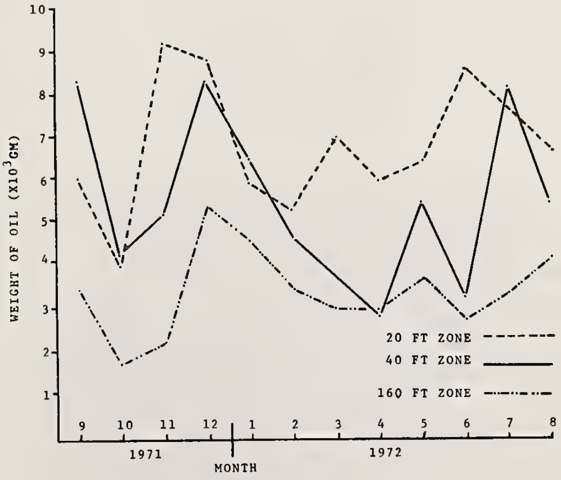

Figure 1. Total monthly weights (gm) of oil from the 20, 40, and 160 feet zones (normalized to 100 feet zones).

Table I. Root Mean Squares Expressed As Percentages Of The Total Annual Oil Loading In The 20 Foot Zone.

	40	80	120	160
20	9.75	11.27	9.98	9.25
40		4.65	7.10	6.57
80			8.42	7.04
120				8.67

The maximum observed difference is 11.27 percent. It is interesting to note that this did not occur between the smallest and largest zones, but rather between the 20 foot zone and the 80 foot zone. These data indicate that a zone as small as 20 feet in length along the beach produced tar accumulation data that was as reliable as a zone eight times as large (160 ft.)

A beach bias is demonstrated in Table 2; proportionately more tar was deposited on the northernmost zones than on the southernmost zones. The reason why more tar should be deposited in one area than in another is not clear until one examines possible climatological influences on tar deposition.

Table II. Zone (Ft.)

	20	40	80	120	160
Total annual oil loading (gm)	15,517	24,133	34,101	42,284	66,384

Figure 2 demonstrates the effect of wind direction on tar deposition. All net wind vectors were calculated by averaging wind direction every three hours over the previous 24-hour periods prior to sampling. Forty-five degree sectors were used; that is, all previous net wind movement vectors between 22.5° and 67.5° were graphed as 45° for each major wind direction plotted. Only those sampling days directly preceded by a sampling day were included in order to negate any build-up effect of tar on the beach.

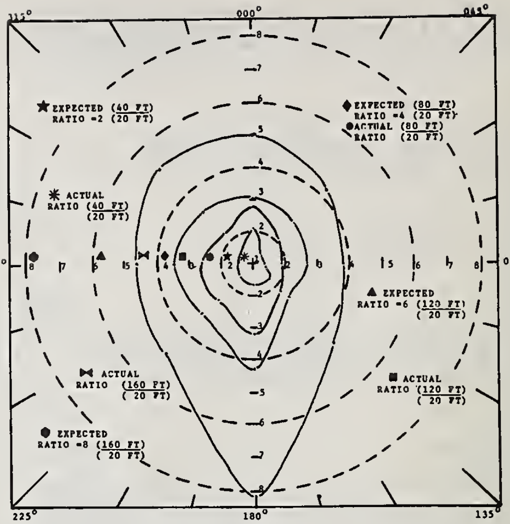

Figure 2. Oil loadings (gm) in the 40, 80, 120, and 160 feet zones ratioed to oil loading (gm) in the 20 feet zone versus net wind direction of 24 hour periods prior to sampling.

The ratios are as expected when the wind was from the south (180°); however, the ratios were distorted when the wind came from either east or west. Essentially this means that east or west winds result in more tar being deposited in the northern end of the sampling tract, than in the southern end. Strong correlation between heavy oil deposition and northeast winds (000° to 090°) is shown in Figure 3.

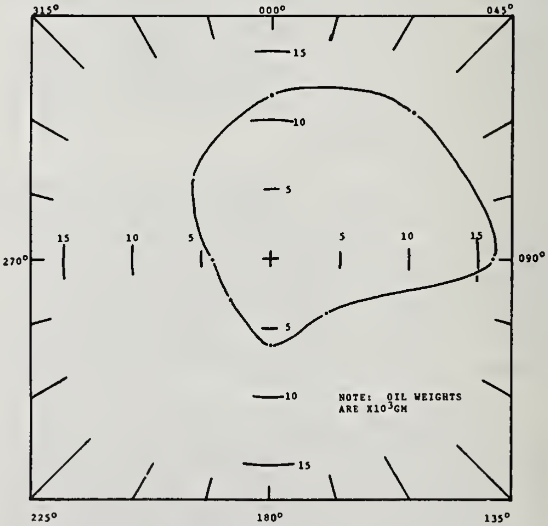

Figure 3. Total oil loadings (gm) from all survey zones versus net wind direction of 24 hour periods prior to sampling.

The expression,

$$A(t) = \frac{r}{k}(1 - e^{-kt})$$

defines the amount of tar present on the beach at any time, where r = rate of tar being stranded, k = constant, t = time in days. Two assumptions were made:

a. The rate at which tar washes ashore is constant.

b. The rate at which tar is removed from the shore is proportional to the amount present on the beach.

Substituting the average of all one-day tar accumulations (737 gms; n = 156) and the average of all three-day tar accumulations (1040 gms; n = 35) into the above equation gives r = 1246 gms/100 linear feet of beach/day, k = 1.162. These values produce a beach time constant (that is, the time necessary for the beach to reach one half the load of tar it will ultimately carry at t = ∞) of .597 days or 14.3 hours, and r/k = 1073 as the assymptotic value: as t approaches ∞, A(t) approaches 1073. In three days this coastal area reaches 97 percent of the maximum amount of tar pollution (by weight) that it will support at infinite time (having started with an initially tar-free beach). The average of all two-day tar accumulations (n=21) produced a value of 759 grams/100 linear feet of beach, whereas the predicted value from the above equation was 968 grams/100 linear feet of beach. This leads one to believe that n = 21 samplings is too small to be reliable. However, since all 3, 4, and 5 day sampling intervals represented the same near-equilibrium tar-loading condition, the average of all such samplings (n= 43) produced a value of 1070 grams/100 linear feet of beach. This is in very close agreement with the value of 1073 grams predicted above utilizing 156 one-day accumulations and 35 three-day accumulations. Therefore, as few as 35 samplings are sufficient to produce an accurate average tar loading value.

Key Words: Equilibrium value, beach time constant, beach bias.

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TAR BALL SAMPLING IN THE WESTERN NORTH ATLANTIC

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Disclaimer: The contents of this report represent the findings and views of the authors who are responsible for the facts and accuracy of the data presented. The paper does not necessarily reflect the official views or policy of the U. S. Coast Guard.

The U. S. Coast Guard conducted a sampling program in the western North Atlantic Ocean beginning in 1971 to determine the quantity and source of floating tar "balls" in the marine environment. Most of the sampling was performed from Coast Guard weather ships deployed at four ocean station sites: Bravo (56° 30' N, 51° 00'W), Charlie (52° 45' N, 35° 30' W), Delta (44° 00' N, 41° 00' W) and Echo (35° 00' N, 48° 00' W) (Figure 1). The series sampling at each location allowed a determination of variability and estimation of the average amount of tar present.

The method used to obtain tar ball samples utilized a neuston net (000 mesh) attached to a fiberglass frame which was towed from the side of the ship. The frame (1.00 x 0.35 m) has a built-in flotation chamber to keep half of the open end of the net above the surface of the water. A mechanical propeller-driven flowmeter was mounted to the lower part of the frame just inside the mouth of the net. The net assembly was attached to an adjustable towing bridle so that the assembly could be adjusted to ride smoothly. The assembly was then rigged to a twenty foot boom located near the bow of the ship. This forward mounting of the boom allowed for sampling from essentially undisturbed surface water.

Towing speeds ranged from drifting to 3.5 knots (1.8 m/sec) with the duration of tow being 45 to 60 minutes dependent on wind conditions. Most of the tows were made during daylight hours. The majority of the tows were made into the winds, although 31% were made perpendicular to wind direction. The sampling system was effective in sea states up to force 6.

All tar balls collected during each tow were individually counted whenever possible and then combined into a single sample. These samples were stored in glass jars having teflon-lined lids and were refrigerated at low temperatures whenever possible. Petroleum smears on the net were noted, but were not included in the determination of tar ball concentrations.

Daily logs were maintained for all tows noting: position, date, time, speed of vessel, duration of tow, meteorological data, sea state, and specific observations with respect to sampling and collected samples.

Tar ball concentrations were determined at a shore-based laboratory and expressed as wet weight of tar (mg) per unit surface area sampled (m^2). In addition the percentage of water contained in all tar balls collected was determined by azeotropic distillation with benzene, and was found to range from virtually none to as much as 51% by weight, with the average being 21%.

A major feature of the data was the extreme variability in tar ball concentrations at all ocean stations except Bravo. The standard deviation in tar ball concentrations was usually of the same magnitude as the sample mean for any series of tows. As an example, a series of 8 tows were made at Echo during a 48 hour period. The tar ball concentrations varied by a factor of 12 in this series of tows. Altering sampling procedures such as tow speed, direction and time of tow, did not decrease this large variability. It appears that the observed variability is due to environmental parameters. A greater knowledge of winds, currents, and waves in the sampling area might explain this sampling variability. A total of 214 neuston tows have been conducted at these four ocean stations. Although the variation in sampling is quite large, certain trends are evident. The concentration of tar balls increases from virtually zero at Bravo to greater than 2.6 mg/m^2 at Echo (Table I). This north to south trend was noted in all three years of sampling. The variation is too large to determine if an increase in tar ball concentrations has occurred at any given ocean station since 1971.

The higher concentrations of tar balls found at Echo is not entirely unexpected. The ocean station is located in the Sargasso Sea. This Sea is bordered by a subtropic anticyclonic gyre. This rotation of the gyre moves surface water toward the center creating a "catch all" basin for floating materials. Assuming that the residence time of tar balls on the ocean surface is reasonably long then one would expect to find a higher concentration of tar balls in the Sargasso Sea.

Key Words: Neuston net, open ocean, tar balls.

Table I. Summary of Tar Ball Concentrations at Four Ocean Stations in Western North Atlantic Ocean (1971 - 1973).

Ocean Station	Range of Concentration (mg/m^2)	Ocean Station	Mean Concentration (mg/m^2)
Bravo	0 - 0.003	Bravo	0.000
Charlie	0 - 1.83	Charlie	0.12
Delta	0 - 10.73	Delta	1.15
Echo	0 - 21.62	Echo	2.64

Figure 1. Location of the four ocean stations in the Western North Atlantic.

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EVALUATION OF THIN FILM OIL SAMPLERS

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Introduction and Objective

Portions of the 1972 Federal Water Pollution Control Act require that the Coast Guard maintain a system for the detection of discharges of oil and other hazardous polluting substances, disseminate information on these discharges, document violations of the act and determine if removal of the oil or hazardous substance is properly done. In order to fulfill its responsibilities, the Coast Guard is developing sampling systems. One of the work units in the sampling systems project is the development of a boat deployable thin film oil sampler. This paper deals with the evaluation of four prototypes which were designed for collecting oil samples from thin films for identification purposes. It is felt that the results and conclusions contained in this paper will be directly applicable to the Marine Pollution Monitoring Pilot Project.

The objective of the tests was to evaluate the samplers':

1. Handling characteristics under practical conditions.

2. Maintenance and repair requirements.

3. Efficiency of oil pickup.

4. Ability to maintain the chemical integrity of the oil.

All of the samplers tested utilized an oleophilic sorbent while two of those tested used a surfactant as well. Figure 1 shows the four samplers which were tested. From the top, clockwise, are Shell Pipeline, Marconsult, Poseidon nets, and Coast Guard R&D.

Figure 1. Collective presentation of samplers.

Description of Samplers

Figure 2 shows the Poseidon Oil Net which is a double layered polypropylene yarn sleeve held open at the mouth by a steel hoop and knotted at the tail. The net is bridled at the mouth and is towed through an oil slick in order to collect a sample. The polypropylene yarn serves as both the oil sorbent and the supporting net material. After a sample is collected, the sampler is simply dropped into a can for shipment to an analysis lab. This sampler is expendable and therefore no cleaning is necessary.

Figure 2. Poseidon oil net.

Figure 3 shows the Marconsult sampler which is a modified stainless steel sieve with top and bottom covers, housing a polyurethane foam pad. The sieve is supported by a chain harness clipped onto the sampler's outer edge. After venting the top cover and removing the bottom cover, the sampler is dipped into the slick in order to collect a sample. After a sample has been taken the bottom cover is replaced and the top cover sealed so that the sampler may be shipped to a lab for analysis.

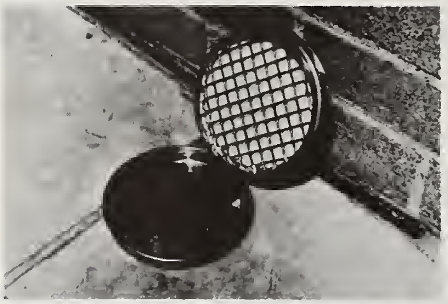

Figure 3. Marconsult sampler.

The Shell Pipeline sampler (Fig. 4) is constructed of corrugated aluminum. Polyurethane foam provides flotation. After saturating the central polyurethane wick with a surfactant, the sampler is lowered into the slick. The surfactant pushes the oil contained by the sampler towards the inside periphery where it is collected by polyurethane strips. After sampling has been completed, the strips are removed and placed into a sample jar for subsequent analysis.

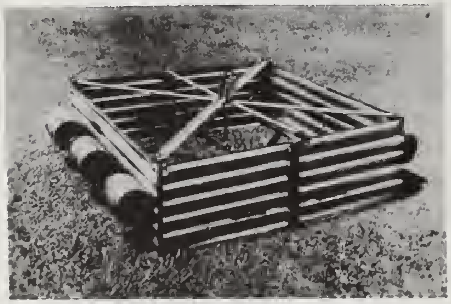

Figure 4. Shell pipeline sampler.

The fourth sampler (Fig. 5) was developed by the Coast Guard's Research and Development Center in Groton, Connecticut. The donut shaped sampler uses a polyurethane wad on a central strut and a surfactant along its inside edge. The sampler is placed in a slick and the surfactant acts to push the contained oil into the center where it is collected by the foam. After the oil has been collected the sampler is removed from the water and the polyurethane placed in a sample jar for subsequent analysis.

Figure 5. Coast Guard R&D Center sampler.

Sea Tests

Sea tests were conducted in order to evaluate the samplers':

1) Handling characteristics under practical conditions.

2) Maintenance and repair requirements.

The oil used during the sea tests was soybean oil. Results of the tests indicated that one of the samplers was superior to the others as far as ease of deployment and maintenance requirements were concerned. This however, was not the only factor involved in the evaluation since tank tests were also conducted.

Tank Tests

The objective of the tank tests was to evaluate:

1) The efficiency of oil pickup of the samplers.

2) The ability of the samplers to maintain the chemical integrity of the oil.

The samplers were tested by deploying them in slicks with nominal thicknesses of 10^{-1} 10^{-2} and 10^{-3}cm. Test oils used during tank tests were a No. 2 Fuel Oil, a Bunker C, and a South Louisiana Crude. The samples collected during these tests were analyzed colorimetrically to determine the efficiency of oil pickup and by gas chromatography, fluorescence spectrophotometry, and infrared spectrophotometry to determine the samplers' ability to maintain the chemical integrity of the oil.

Tank Test Results

The following conclusions were reached after analysis of the tank test results:

1) All of the oil absorbent materials tested contained extractable chemical compounds.

2) Both fluorescence spectrophotometry and gas chromatography appear capable of oil identification through comparison of "fingerprints" of oil samples to "fingerprints" of the original oils.

3) Infrared spectrophotometry is only capable of oil classification under these tests conditions.

4) For the express purpose of characterization of the source of an oil sample (identification), the use of a solvent to extract the absorbed oil should be avoided. If the quantity of absorbed oil permits mechanical removal, then this technique should be used since chemical characterizations are enhanced.

5) The surfactant used did not interfere with the identification of the test oils.

Determination of Overall Ranking

The results of the sea tests and the tank tests were assembled and the samplers were ranked in the following categories: infrared, gas chromatography, volume of oil collected, efficiency of oil collection, sea tests, fluorescence, and sampling time. It was felt that neither fluorescence nor sampling time discriminated between samplers to a sufficient degree to justify rankings. Therefore, all samplers were assigned equal scores in these categories.

The overall ranking of the samplers (Table I) indicates that the Coast Guard R&D sampler was best, but it is recognized that there is room for improvement. It is further recognized that the substitution of one sampler's foam for another's would probably result in some change in the finishing place for those samplers.

TABLE I
OVERALL RANKING OF SAMPLERS

SAMPLER	RANK	INFRARED	GAS CHROMATOGRAPHY	VOLUME OF COLLECTED OIL	EFFICIENCY OF OIL COLLECTION	SEA TESTS	FLUORESCENCE	SAMPLING TIME	AVERAGE SCORE
R&D	1st	1	2	4	1	3	2.5	2.5	2.29
MARCONSULT	2nd	2	3	3	2	2	2.5	2.5	2.43
SHELL	3rd	3	1	1	3	4	2.5	2.5	2.43
POSEIDON	4th	4	4	2	4	1	2.5	2.5	2.86

Conclusions and Recommendations

In designing a technique for oil sampling, consideration must be given to the techniques by which the sample will be analyzed. The sorbents used in all of these samplers contained extractables which interfered with analysis. The matter was further complicated by a variation in extractables from manufacturer to manufacturer as well as from lot to lot.

Although improved quality control or pretreatment of suspected source samples might alleviate the problem, elmination of the source of the contaminants is recommended.

The Coast Guard's present efforts are directed towards the substitution of glass wool for the sorbent and the elimination of solvent extraction. The following recommendations are specifically addressed to the development of an oil sampling technique for the Marine Pollution Monitoring Pilot Project:

1) Sorbents such as polypropylene and polyurethane should be avoided.

2) If sorbents are used (due to their high oil collection efficiency) infrared spectrophotometry can not be used for identification of the samples. Gas chromatography and fluorescence spectrophotometry appear capable of identification under these conditions.

3) Solvent extraction should be avoided; if the quantity of oil absorbed is sufficient, mechanical removal is preferable.

4) Glass wool may be used as a collecting medium. If glass cloth is used it must be of the untreated variety as the treated variety contains potential contaminants.

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Key Words: Oil sampling, Sorbents, Surfactants, Oil identification.

Appendix A - Infrared Spectrophotometry

Infrared studies were performed using a Perkin-Elmer 567 Spectrophotometer in conjunction with a Wilks FMIR beam condensing attachment. The KRS-5 crystal was dipped repeatedly into cyclohexane solutions of the absorbed oils. Blank cyclohexane extracts of the sorbents were also run. The residues coating the plate after evaporation were analyzed. Interpretation of the infrared traces was made primarily by examination of the "fingerprint" region from ca. 1300 - 600 cm^{-1}, with particular attention to the 880 - 700 cm^{-1}region.

Appendix B - Ultraviolet Fluorescence

A Perkin - Elmer MPF-3 Fluorescence spectrophotometer was used. Spectra were run on the cyclohexane/oil solutions eluted from the absorbents. Blank cyclohexane extracts of the sorbents were also run. The emmission spectra from 260 - 500 nm were obtained with 254 nm excitation.

Appendix C- Gas Chromatography

A Varian Gas Chromatograph Model 2800 was used. Chromatographs were programmed from 75° C to 275° C @ 6°/min. The column was 5 x 1/8" S. S. packed with 3% SE-30 on Variport (100/120) mesh. 10 μl of the oil in cyclohexane mixture was injected. The carrier gas was helium. Blank cyclohexane extracts of the sorbents and pure cyclohexane were also run.

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OIL SPILLAGE MONITORING, SAMPLING AND RECOVERY SYSTEMS

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Products have been developed by Durham Associates, Inc. for use in controlling marine pollution from petroleum. They incorporate a unique selectively transmissive membrane which, while preventing the penetration of water, allows oil to flow through easily. Modifications of this membrane have been used in the construction of oil spill detection systems, oil recovery devices, and surface oil samplers.

The purpose of this symposium is to discuss and plan a program to evaluate marine petroleum pollution. It will be a comprehensive program monitoring several forms of oil pollutants over large areas of water. Pollution baselines will be determined. The most important information which should be gained from the survey is to ascertain the sources of the marine oil pollution. Without determining and controlling the entrance points of the oil into the environment, the environmentally conscious community can only look with despair at the climbing oil pollution baselines. Once the potential sources have been determined, they should be monitored continually to reduce the damage to the environment. With the proper monitoring procedures, a potential 10,000 gallon oil spill can be prevented before only one gallon has reached the water. Economically, those involved in the cleanup of oil pollution find that the cost of removing equal volumes of oil from water increases almost exponentially with the residence time of the oil in water. The relative ease of removing 500 gallons of oil just as it enters the plant effluent stream can be appreciated when compared to trying to remove the same 500 gallons once it has dispersed in the harbor.

The basic technology of the oil spillage monitoring, sampling and recovery systems developed by Durham Associates, Inc., centers on the hydrophobic, lypophilic properties of certain materials. Surface properties of a porous substrate are adjusted so that the water does not wet the surface of the pores. In equilibrium, the propensity of a liquid to wet a solid surface is determined by the following equation:

$$\gamma_{LV} \cos\theta = \gamma_{SV} - \gamma_{SL}$$

where γ is the surface free energy, LV is the liquid-vapor interface, SV is the solid vapor interface, SL is the solid-liquid interface and θ is the contact angle of the liquid with the solid surface. By modifying γ_{SV} and γ_{SL} , the angle θ can be affected for a given liquid. It is desired that water not wet the membrane so θ is made greater than 90° for water.

The standard capillary rise equation for a cylindrical capillary is:

$$\Delta P = (2\gamma \cos\theta) / r$$

where ΔP is the pressure difference across the liquid-vapor meniscus; γ is the liquid vapor surface tension; r is the radius of the capillary and θ is the contact angle of the liquid with the solid. If θ is greater than 90°, then $\cos\theta$ is negative, causing ΔP to also be negative. In this case the liquid is retarded from entering the capillary by the negative pressure. This phenomenon is called capillary depression and is the means by which the membrane in the devices herein discussed retards the penetration of water.

Oil, on the other hand, has a contact angle of less than 90° with the pore surface. The pressure across the oil-vapor meniscus is positive, causing the oil to flow into the pores. Once into the membrane pores, the oil will continue to flow through the membrane. In this manner the membrane will continuously separate oil from water by allowing the oil to pass through the porous substrate but retarding the passage of water.

The oil spillage detection system incorporates this unique membrane to constantly monitor the water's surface for oil slicks. The membrane is floated at the air-water interface so that any oil on the surface will contact the membrane. Once at the membrane surface, the oil enters the pores and flows through. The oil which has passed through the membrane collects in a small receptacle where the presence of the oil is detected by a float activated switch. The float switch is a simple device and the single moving part in the system. A float, shaped to the contour of the receptacle normally rests on the receptacle floor. As oil flows in, the float lifts, moving an integral permanent magnet in relation to a hermetically sealed SPDT magnetic reed switch. When the preset alarm threshold oil quantity has been accumulated, the switch is actuated, transmitting a real-time alert and initiating a desired chain of events. The detector communicates the presence of oil to a monitor by wire or by VHF radio transmission

The oil spillage detection system requires no electrical power or human effort until an oil spill has been detected. It constantly monitors the water's surface independent of lighting and weather conditions. A small sample of oil is collected so that it may be analyzed to determine the source of the pollution.

The same basic technology is used to make effective clean-up devices. While the liquid collected by many present oil spill collection devices contains a large percentage of water, a recovery device incorporating this selectively transmissive membrane collects oil which is virtually free of water.

One such configuration suitable for bilges and ballast tanks contains a membrane in a fluted cylindrical configuration. The containment receptacle again contains a float switch, but in addition to transmitting information as to the volume of oil being separated, it activates a pump which transfers the oil from the containment receptacle to a larger holding tank. Flow rates of 500 gallons per hour are possible with the system.

Another recovery system design which requires no power incorporates a floating skimming head with the selectively transmissive membrane and a suitable container which are connected, but which may float independently. The skimming head always floats at the air-water interface. The oil which enters the head flows by gravity into the container. The container is so ballasted that the level of oil is always below that on the water surface. By monitoring the height of the container in the water it can be determined how much oil has been recovered.

The ultimate objective of the Marine Pollution Monitoring Symposium is to reduce the amount of oil entering the world's streams, lakes and oceans. As a means to that end, we feel that it is of utmost importance to provide an early warning of spilled oil and immediate clean-up. Timely detection and clean-up is the key to reduction of environmental damage by petroleum.

Key Words: Oil Detection, Oil Sampling, Oil Recovery, Selective Membrane.

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SAMPLING OF OIL SPILLS AND FINGERPRINTING BY INFRARED SPECTROSCOPY

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Infrared spectra of crude oils and their various distillates in the 650 to 1200 cm^{-1} region provide unique fingerprints, which can be used to identify the source of oil slicks. An example of the differences in the spectra of three No. 2 fuel oils is shown in figure 1. Most No. 2 fuels have the same bands in this spectral region; however, the relative intensities of the bands are characteristic of each individual sample and these are used to fingerprint the samples.

A computer data bank has been set up for petroleum samples from known origins. Per cent transmission for 21 selected bands in the 650 to 1200 cm^{-1} spectral region are converted to absorptivities, and the absorptivities are stored in a computer file [1]. At present, we have data for over 100 samples stored in this data bank.

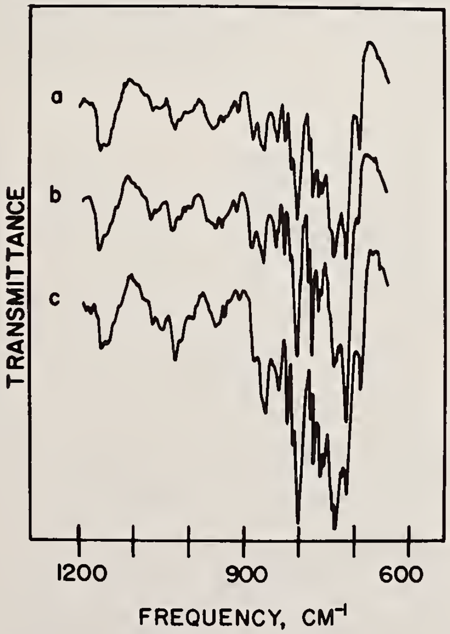

Figure 1. Infrared spectra in the 650 to 1200 cm^{-1} region of three No. 2 fuel oils: a, Delta; b, Zaire; c, domestic.

To match an oil from an unknown origin with the correct known stored in this data bank (assuming that data for the known is in the data bank), the spectrum of the unknown is measured, and the per cent transmission for the 21 selected bands are converted into absorptivities. A computer program then performs the following steps:

i) Ratios of absorptivities of each known to those of the unknown are calculated

ii) Average ratio of each known to unknown calculated

iii) Ratios divided by average to make average 1.0

iv) Difference between ratios and 1.0 (the average) calculated

v) List the number of bands for each known with a difference (ratio - average) less than ±0.05, ±0.10, ±0.25 and ±0.50.

In comparing the unknown to the correct known, the ratios of absorptivities of known to unknown would have values equal to or very close to 1.0, since they are in essence the same substance. Deviation from the value of 1.0 (the ideal average ratio) for each band gives a measure of deviation from a "good match" or "positive identity" of the unknown.

The method has been tested on several oil slicks during the past year. On one occasion a tanker leaked 100,000 gallons of No. 6 fuel oil into Narragansett Bay. A quart sample was obtained from the tanker. This sample was fingerprinted and the spectral data stored as a known in the data bank. Samples were collected from the Bay and the beaches during the next four weeks. These were treated as unknowns in the identification method and in all cases they matched with the sample from the tanker [2]. A month after the original spill a slick (II) came ashore 10 miles from the original spill, and it was reported in the local papers that this slick was due to the tanker spill. However, our analysis showed that it was from a different source. Two months after the tanker spill, another slick (III) was sited in Narragansett Bay. Our analysis showed that these latter two slicks were from the same origin, and we eventually found their source.

The question arises as to how well the method works for light fuel oils. It has been tested on a No. 2 fuel oil which was weathered on a fresh water pond. A local industry was leaking oil onto a pond through a storm drain system. The industry had 13 different petroleum products stored at their plant site. The spectrum of the oil indicated that it was a No. 2 fuel; however, there were three No. 2 fuels stored at the plant. The spectrum of the pond sample was close to one of a No. 2 fuels found in an old underground tank. This tank was excavated and several holes were found in it. Oil had not been stored in the tank for several years, so the tank could not be directly responsible for the present source of oil. Boring holes were drilled in the area of the tank, and eventually an underground pool of oil was located. This pool had built up over the years, and leaked into the storm drains. During this investigation oil was collected from the storm drains by directing the water over aluminum foil. During a 24 hour period we were able to collect 20 ml of oil by this method.

Much of our sampling of oil slicks and floating films has been done by the Al foil technique [3]. Oil adheres to the foil and water is repelled. The foil can be returned to the laboratory, and the spectrum of the oil measured without removing it from the foil.

Currently, the infrared technique is being tested on all types of petroleum weathered in floating containers on Narragansett Bay, weathered on sea water on the roof of our laboratory, and on sea water under artificial conditions in the laboratory.

In addition to oil slicks, we are measuring the infrared spectra of oil extracted from sea water. Spectra of samples as small as 300 μg of oil have been measured (spectra of 30 μg samples of laboratory chemicals have been measured, but at present we have not measured spectra of petroleum in these small amounts). Currently, we are measuring the spectra of organics extracted from water in a local pleasure craft harbor. We have been monitoring this harbor all winter, so that the increased amounts of lubricating oils can be detected during the summer months.

We have also measured the spectra of tar ball samples and extracts of tar balls. The infrared spectra show that the major difference in tar ball samples is the ratio of paraffins to aromatics present.

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A NEW INFRARED INSTRUMENT FOR MONITORING OIL FILMS ON WATER

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A new infrared instrument for detecting and monitoring oil films on water surfaces is currently being evaluated and improved in a program funded by the United States Coast Guard Office of Research and Development in Washington, D.C.*

The automatic remote detection device utilizes a technique based on the infrared reflectance properties of water surfaces. As shown in Bramson [1], water surfaces exhibit unique properties of infrared reflectance at the 3 micron spectral region where sharp changes in reflectance occur due to absorption bands of water molecules. In this region, a change in reflectance of almost 500% occurs for a 10% change in wavelength. Figure 1 shows the reflectance dropping from approximately 2% at 2 microns to a valley of 0.75% at 2.7 microns, and then rising sharply to a peak of 4.7% at 3.07 microns before returning to approximately 2% at 4 microns.

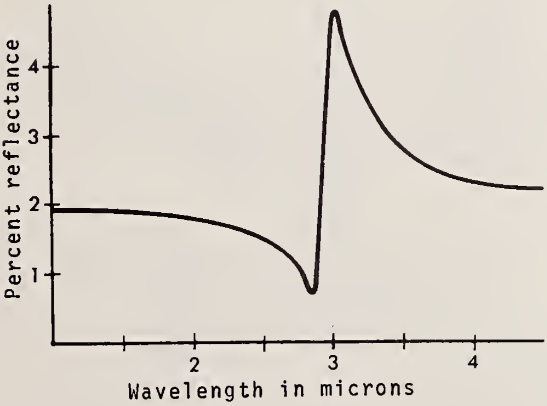

Figure 1. The spectral reflectance of water surfaces.

The reflectance spectrum of oil films differs from that of water surfaces in an unambiguous manner when viewed in the 3 micron region. Hydrocarbons do not exhibit the deep valley at 2.7 microns and the adjacent sharp peak at 3.1 microns. The peak and valley for water surface reflectance can be expressed as a ratio of approximately 6:1; the same ratio for oil film reflectance is approximately 1:1. By monitoring the infrared reflectance of water surfaces at the 3.1 micron peak and the 2.7 micron valley and computing a ratio from these readings, the presence or absence of a hydrocarbon film can be immediately detected.

An Infrared Oil Film Monitor consists of a transmitter and a receiver. When the compact instrument is placed above and perpendicular to the water surface to be monitored, a beam of infrared light is transmitted to the water surface and reflected back to the receiver. The reflected light beam passes through two optical interference filters mounted in a rapidly rotating filter wheel and the resulting signals are electronically processed to provide two reflectance readings (at the peak and valley described above) and a reflectance ratio from those two readings. An alarm is activated when the normal ratio decreases to a predetermined value indicating the presence of an oil film on the water surface.

An evaluation program was begun in early 1973. Testing of the Infrared Oil Film Monitor was accomplished in both laboratory and field environments and the instrument's oil detection abilities were extensively documented [2]. Laboratory tests verified that the 3.1/2.7 micron ratio did not significantly respond to changes in water type or to non-hydrocarbon pollutants introduced into the test pools. However, the ratio consistently dropped whenever a hydrocarbon film was present on the water surface. Measurements showed that the instrument responded to hydrocarbon film thicknesses of 0.1 microns or greater.

Effects of the marine environment on the instrument's performance were tested during several months of continuous use while mounted six feet above the water surface on the bow of a 40-foot research boat. The water surface of a congested commercial harbor was monitored both while underway and with the boat docked in the inner harbor.

The following observations were made on the performance of the Infrared Oil Film Monitor in the field. The instrument's performance was independent of ambient lighting conditions - operating 24 hours a day. Oil detection abilities were not deteriorated by heavy rain, fog, or high humidity. The instrument did not "false

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[*] The opinions or assertions contained herein are the private ones of the writers and are not to be construed as official or as reflecting the views of the Commandant or the Coast Guard at large.

alarm" at fish and vegetable oil films on the water surface, yet it was not hypersensitive to trace concentrations of hydrocarbons almost always present in commercial harbors. Independent gas chromatographic analysis verified the instrument's detection and false alarm discrimination capabilities in the field environment.

Possible applications for the Infrared Oil Film Monitor include: continuous monitoring of water surfaces at petroleum loading areas, offshore platforms, and refineries; crisis monitoring of oil spills when weather conditions exclude aircraft surveillance; detection of polluting discharges for law enforcement; and scientific research and surveys.

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Key Words: Infrared Oil Film Monitor; infrared reflectance; ocean pollution detection; oil film detection; oil pollution; remote sensing; water surface monitoring.

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MAPPING AND IDENTIFICATION OF OIL ON WATER BY THE USE OF AN AIRBORNE LASER SYSTEM

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Airborne laser oil fluorosensor systems have been test flown both here and elsewhere for the detection of oil on water [1, 2]. Recently there has been increased interest in developing an advanced model which not only detects but also performs a broad classification of the target oils according to their grades. So far a proven method has been to scan the laser induced emmission spectrum in relatively slow serialized manner at the rate of one cycle per second using a spectrometer and image dissecting tube [3]. In order to overcome both problems of spectral and spatial resolutions necessary for the application from a relatively high speed aircraft, NASA Wallops is investigating the use of a 500 parallel optical multichannel analyzer (OMA) for a laser oil fluorosensing technique.

The block diagram of figure 1 pertains to the NASA unit which has both real time display for immediate action, and digital tape storage to use as later reference. The system uses an Avco pulsed nitrogen gas laser. The laser provides a nominal 1 mj 337 nm ultra violet radiation in 10 nsec. The repetition rate of the laser is set at 30 pulses per second as the OMA's data transfer to a mag tape unit requires 33 msec per cycle.

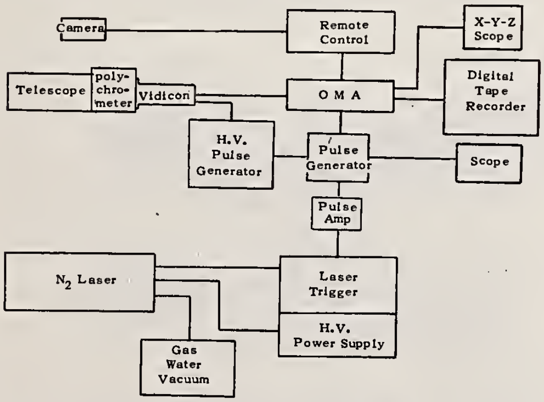

Figure 1. Block Diagram of Airborne Laser Sensor

The receiver optics consists of a 15 cm diameter f-3.2 Cassegranian telescope mounted on a .3 m polychromator. The output spectrum is focused on the face plate of a silicon intensified vidicon television camera which is gated on for 0.1 to 1 μsec by a high voltage pulse generator. This gating in turn is also driven by the OMA data cycles and time delayed so as to pick up the return fluorescent signal. With this arrangement, the system works just as well as in the day time as it does at night.

Video information is processed in the OMA for real time CRT display and converted to BCD for 9 track tape storage. Any preset number of scans may be accumulated in the OMA memory buffer before dumping on tape. Also, the signal information may be subtracted from a background signal before dumping. The whole system is operated from a remote control to simplify operation and a 35 mm wide angle camera photographs the area to be mapped.

The OMA system was calibrated against a NBS standard tungsten filament lamp as shown in the arrangement of figure 2. A collimated beam of known intensity was directed toward the receiver, placed 30 m away and measurements consisted of a set of readings in continuous accumulation and gated modes.

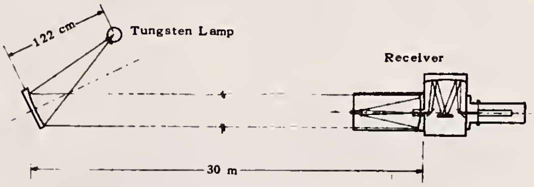

Figure 2. Calibration Apparatus

The following table shows calculated sensitivity of the OMA vidicon tube in the system from the experiments.

Wavelength	Maximum OMA Sensitivity
450 nm	90 photons/count
475 nm	45
500 nm	36
550 nm	40
575 nm	44
600 nm	42

In reality, one has to take into consideration the loss factor due to the spectrometer efficiency, therefore acceptable efficiency figure should be in the order of 100 to 300 photons per count. In order to test the system's capabilities, it was first tried in the lab. A pan of water was placed on the floor and the different grades of oil films were made on this. The laser and receiver were placed at a distance of 10 to 15 m down the hall, with a large mirror placed directly above the water pan to deflect the light toward the laser sensor. Single cycle dumps for 10W30 motor oil, 90W motor oil, and oil with coumarin dye additive are shown in figures 3, 4, and 5. This data was taken with a .6 mm slit with a 500 nsec gating pulse width and the SIT tube voltage of 9 kv across the tube. These laboratory measurements and calibrations show that the instrument is capable of

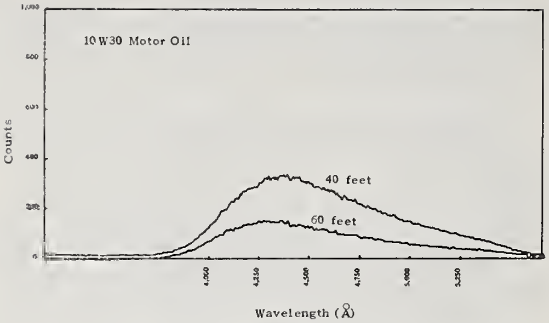

Figure 3. Laser Induced Emission from 10W30 Motor Oil

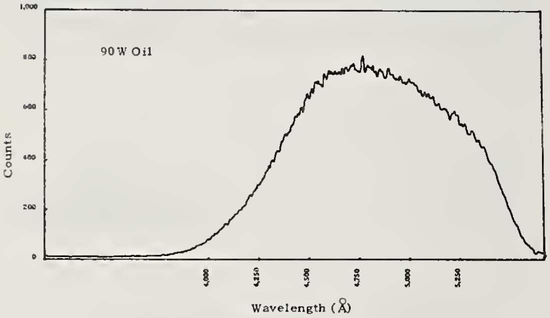

Figure 4. Laser Induced Emission from 90W Motor Oil

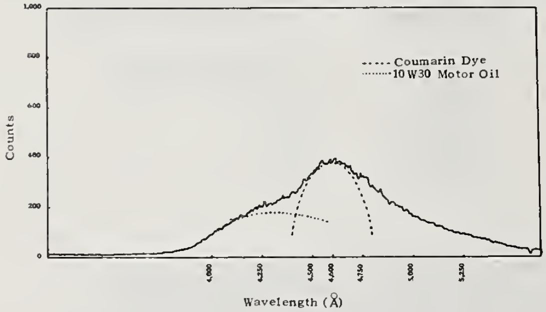

Figure 5. Laser Induced Emission from Oil with Coumarin Dye Additive

detecting different grades of oils at shorter distances. For the radiative transfer equation of lidar,

$$\text{Power Received} = \frac{(\text{Area of Receiver})(\text{Power Transmitted})\ (\text{Q.E.})}{(\text{Range})^2},$$

one would expect that at 100 m altitude, the fluorescent signal reaching to the entrace slit of polychromator would be approximately in the order of 10^6 photons in the visible region. The Avco laser delivers about 1.5×10^{15} photons of 337 nm per pulse, and the Quantum efficiency of laser induced fluorescence is taken as .1%. Our experiences with OMA show that roughly 10^5 counts are needed for a good spectral signature in one scan. If the light in one pulse is sufficient for a spectral signature, oil spills as small as 2.7 m across in size can be detected and catalogued from an aircraft traveling at the speed of 300 km per hour. These performances do seem to meet the requirements set by law enforcing agencies to determine the type of oil pollution to use as presecuting evidence from aircraft.

Already certain improvements can be visualized over our present OMA system, if the system were to be used for operational purposes: a) Physical dimensions of the transmitted laser beam and the entrance slit to the polychromator should be constructed to match the images so that a maximum signal to noise ratio be attained. b) Since the emission spectra of oil derivatives are in broad bands, the present 500 channels output, 0.5 nm per channel resolution, seems to be almost redundant. The total fluorescence counts can be divided among 20 channels, 10 nm per channel, and computer aided pattern recognition o: the peak and shoulder channels can be performed instantaneously on-board. This problem we believe is strictly software nature. c) In order to increase further gain on the sensitivity, it is possible to use a higher gain SIT tube available on the market today. The final design parameters and other operational details will be determined only after the completion of extensive airborne field tests of this system. It is our intention in this presentation to show that such a technique can be available for global oil surveillance in the near future.

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Key Words: Airborne Laser Oil Fluorosensor, Remote Detection, Spectral Signatures.

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MOVEMENT OF SPILLED OIL IN SAN FRANCISCO BAY AS PREDICTED BY ESTUARINE NONTIDAL DRIFT

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Introduction

From March 1970 through April 1973, the U. S. Geological Survey released surface and seabed drifters every 2 months within San Francisco Bay and on the continental shelf of central California as a part of a study of seasonal nontidal drift patterns in the Bay (fig. 1). One of the routine release points was located at the site of a major oil spill which occurred on 18 January 1971 when two oil tankers collided at Golden Gate, San Francisco Bay, California (fig. 2). Approximately 3200 m^3 (26,700 barrels) of Bunker C fuel oil spilled into the bay [1].

Marked similarities between the drift patterns of the spilled oil and that of both the surface and seabed drifters became immediately obvious. These similarities, together with 3 years of data from the drifter study made it possible to predict the movement of spilled oil.

Figure 1. The San Francisco Bay region and environs. Suisun, San Pablo, and San Francisco Bays constitute the bay system. North, central, and south bay designations are also commonly used.

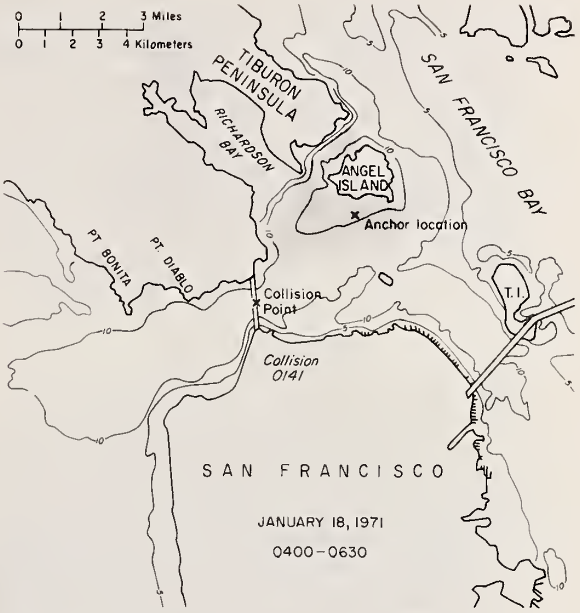

Figure 2. Approximate distribution of oil slick between 3 and 5 hours after the collision. The collision point and anchor location of leaking tanker is indicated. U. S. Coast Guard observations; redrawn from [4], page 130. Water depths expressed in fathoms.

Drifter Movements

The drifter used in these studies is a saucer-shaped plastic disc on a plastic stem [2]. The drifters float just under the water surface and consequently follow the surface currents (surface drifters). With the addition of a brass weight the drifters become seabed drifters and move with the near-bottom water [3]. More than 40,000 drifters have been released; usually 20 to 25 percent are recovered from each release.

Preceding and following the January 1971 oil spill, drifter movements in the estuary and adjacent ocean during December 1970-February 1971 (figs. 3 and 4) portrayed typical winter nontidal drift conditions of near-bottom and surface waters [3]. There was well-defined estuarine circulation in north bay and in the Gulf of the Farallones (figs. 3 and 4). In north bay the near-bottom drift convergence occurred in the shoals in the vicinity of Point Pinole. South bay experienced a surface drift northward out through Golden Gate, and a weak near-bottom drift southward in response both to density-induced circulation and to occasional southeasterly winter storm winds. Seaward, the north-setting Davidson Current was well developed (fig. 4).

Figure 3. Release and recovery points for seabed drifters in the bay system and adjacent Pacific Ocean. Drifter movements are shown as arrows drawn from release points to recovery locations and portray simplified paths of movement; 1200 released and 15 percent recovered within 2 months. Modified after figure 5 in [3].

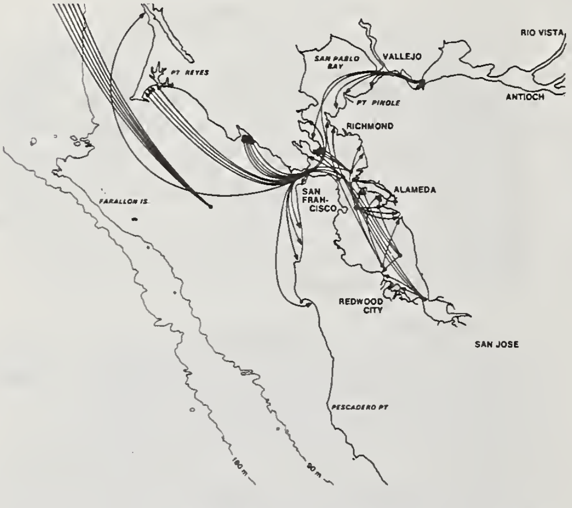

Figure 4. Release and recovery points for surface drifters in the bay system and adjacent Pacific Ocean. Drifter movements are shown as arrows drawn from release points to recovery locations and portray simplified paths of movement; 825 released and 33 percent recovered within 2 months. Modified after figure 6 in [3].

The Oil Spill

The oil spill occurred at 0141 PST during a flooding tide [1,4]; the bulk of the oil spilled within central bay began to drift seaward on the following ebb tide (fig. 2). By 1200 PST, oil had drifted several kilometers seaward of Golden Gate. The main slick bifurcated, one portion drifting southward and the other portion drifting northward. Seaward of Golden Gate, oil eventually beached as far south as Pescadero Point and as far north as Point Reyes. The largest amount of beached oil was found north of Golden Gate in the Stinson Beach-Duxbury Point-Double Point area (fig. 1). Within the bay, beached oil was observed as far south as the San Francisco wharf area and as far north as Point San Pablo and Point San Quentin. Oil that did not immediately drift seaward remained in the vicinity of Angel Island for 3 to 4 days, gradually diminishing in abundance.

There was evidence that some of the spilled oil, in the form of plum- or spindle-shaped tarry globules (ranging from 1 to 3 cm in diameter and as much as 7 cm in length) had sunk. Globules were variously seen moving along the bottom of the bay and adjacent ocean, surfacing, or washing onshore with succeeding tides. Further evidence that oil had sunk was provided by staining of seabed drifters by oil: seabed drifters released 3 weeks before the spill were found oil-stained on oil-free beaches (fig. 5) several weeks after the spill.

Figure 5. Release and recovery points for oil-stained seabed drifters. All drifters were released from 21 to 23 December 1970, and recovered between 18 January and 26 February 1971. No drifters released during December were recovered oil-stained until 18 January.

The spilled oil sank, apparently after it gained density by loss of its lighter hydrocarbon fractions by evaporation and solution [5,6,7] and was mixed through the water column by the strong tidal currents and wind. Oil globules, carried downward because of the water turbulence that extends to the bottom at Golden Gate, were apparently mixed with the sandy and gravelly bottom sediments, and so weighted, remained near the bottom. These observations have reinforced a growing awareness [5,8,9,10] that spilled oil can sink.

Similarity of Drifter and Oil Movements

Trajectories of surface drifters generally agreed both temporally and spatially with the gross oil dispersion patterns. Surface drifters released at Golden Gate and within the Bay system were recovered in coastal areas where the oil beached. There was also a similarity in the relative quantity of beached oil and drifter recoveries: most of the drifter recoveries made shortly before and after the spill occurred in areas where the heaviest concentrations of oil beached.

Data from the stained seabed drifters not only present additional evidence that oil sank, but also give some indication of the probable direction of the movement of the sunken oil (fig. 5). Seabed drifters released in the Gulf of the Farallones 3 weeks prior to the oil spill were found in San Pablo Bay. The most heavily stained drifters were found in the vicinity of Point Pinole, where oil was seen on the beaches several weeks after the spill. However, it should be noted that some of the oil-stained seabed drifters were recovered on sections of beaches that remained oil-free, suggesting that they were stained by oil at depths. Oil on the Point Pinole beaches was apparently transported along the bottom by near-bottom drift, as were the accompanying seabed drifters. This is suggested by the fact that the shoreward limit of beaches stained by floating oil (observed shortly after the spill) was 16 km to the west, toward Golden Gate [11].

Predictions

The foregoing presents evidence for the landward transport of sunken oil by (nontidal) estuarine circulation. Studies of the transport of other substances in estuaries [12,13,14,15] indicate that such transport of sunken oil should occur. This process of nontidal water movement (both seaward surface drift and landward near-bottom drift) is fundamental in predicting pathways that may be taken by oil spilled in or adjacent to estuaries.

Correlation between drifter and oil movements permits prediction with relative certainty of movements and behavior of oil spilled in San Francisco Bay at varying times and locations. The dominant direction of oil drift from any injection point can be determined from figures 3 and 4. Indeed, figure 4 (figs. 6 and 8 in [3]) is used as a basis for a plan of preparedness in cleaning up future oil spills in the bay [16]. In addition, prediction of oil drift at various seasons of the year can be based on existing drifter studies [2,3, unpublished data].

Future Outlook

This experience in San Francisco Bay has shown that basic knowledge of water mass movements in coastal areas is of paramount importance in predicting spilled oil dispersal patterns. Our drifter program, although yielding only empirical answers in the initial stages of the experiment, has been useful for describing seasonal currents in coastal waters. Similar studies would be of great assistance in determining currents in coastal areas where oil spills may occur.

Oil sinking mechanisms (i.e. great water turbulence and high suspended particle concentrations as well as evaporation and solution of light hydrocarbon fractions) are commonly found in nearshore and inshore waters; this implies that oil commonly sinks, and that skimming of oil from the water surface may not guarantee adequate removal of all spilled oil. Furthermore, in light of the landward transport of sunken oil into estuarine systems, removal of floating oil in the coastal zone by deliberate sinking (i.e. powdered chalk, etc.) seems unwise.

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Key Words: Estuarine circulation, nontidal drift, oil spills, San Francisco Bay, seabed drifters, surface drifters.

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OIL POLLUTION ALONG THE INDIAN COASTLINE

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SUMMARY

Oil in the form of tar balls is washed ashore along the Indian beaches. These were first noticed in 1970 (1). From 1971 to 1973, studies were undertaken along both east and the west coasts of India to determine the areas, seasons, and the intensity of deposition of tar balls and their possible origin, Figure 1.

The size of the tar balls, places and seasons of deposition vary a great deal. Therefore, for comparison of data from selected beaches, duplicate samples were collected from 0.1 m^2 surface at supra, high, mid and low tide marks and the weight of tar balls was determined and expressed as g/m^2.

The extraneous material associated with tar balls give some indication of their origin. Therefore, the associated material like debris, plastic beads and polychaete tubes etc., were also noted. In addition, the nature of beach (sheltered or open), its gradient and intertidal exposure were also measured.

A part of the west coast of India, from Ratnagiri to Karwar, was selected as a principal sector for repeated observations. Other beaches located along the west coast from Bombay to Porbander, and from Calicut to Trivandrum; were kept for single observation. Similarly, some beaches along the east coast of India, from Rameswaram in Tamil Nadu to Ongole in Andhra Pradesh, were studied only once. Repeated coverage of selected beaches gave the intensity and seasons of pollution whereas from the other areas an estimate of the extent to which the Indian coastline is affected by the deposition of tar balls could be made.

The tar balls were at first noticed in 1970 at the Vagator beach, Goa. During 1971, 6 beaches were inspected in Goa, of which 4 had tar balls. At the Calangute beach at the supra tidal area the deposition was heavy.

During 1972, the beaches of the 550 kms coastline on the west, from Ratnagiri in Maharashtra to Mangalore in Karnataka State were studied.

In Maharashtra of the 7 beaches studied, 6 had tar deposits. In Goa, 3 beaches - Anjuna, Baga and Calangute - had fresh tar deposits at low, mid and high tide marks. But in the southern part of Goa, i.e., at Colva beach no tar balls were seen. In the Karnataka State, from Karwar to Malpe, of the 11 beaches, examined, 8 had heavy deposition of tar balls at mid and high tide marks.

Along the east coast, during September 1972, 20 beaches in Tamil Nadu were inspected. Of these 7 were sheltered beaches in the Palk Bay and 13 were open beaches north of the Palk Bay. In the Palk Bay, mostly at the high tide mark, tar balls in small quantities were found at 5 beaches only. North of the Palk Bay, 10 beaches had moderate deposition of tar balls.

In the Andhra Pradesh, of the 5 open beaches, only 2 had moderate deposition of tar balls. All the 5 beaches were away from any estuarine influence.

At Point Calimare where the beach area was large, the tar balls of different sizes were found in supra littoral region. These were solid tar lumps mixed with sand and were probably washed ashore during December-January of the previous year.

In 1973, along the west coast, 60 beaches were studied, of which 58 were found to be polluted. The details for each state are given in table I.

Table I. Deposition of tar balls observed during 1973 in various maritime states along the west coast of India.

	Gujarat	Maharashtra	Goa[a]	Karnataka[b]	Kerala[c]
Beaches:					
Observed	5	10	14	11	19
Polluted	5	10	14	11	17

[a] See Figure 2.
[b] See Figure 3.
[c] See Figure 4.

In Meharashtra and Goa, tar deposition started during the last week of May. In the third week of June, all of a sudden heavy deposition was seen.

The process of deposition was studied et Goa beaches on 23 June, 1973. Fresh end small tar lumps were first seen floating in water. With the incoming tide these were washed ashore. The size of tar balls varied from 1 to 4 mm. At first they were deposited at low tide mark but with the rising tide they were pushed higher up and ultimately came to lie at the high tide mark. At Sinquerim which is nearer to Marmugeo Harbour, the intensity of deposition was as high as 4,480.0 g/m^2 and along the northern direction away from Marmugao Harbour, the intensity decreased. The details of deposition at some beaches are given in table II.

Along the Indian coastline oil pollution in the form of tar balls occur in many parts. On the west coast deposition starts with the approach of monsoon season i.e., in the months of May and June. Along the east coast tar deposition appears in December and January.

The deposition is not uniform. At some places, parts of the beaches in between the two levels of tar deposition, were completely free from tar. Maximum deposition occurred at the high tide mark. Sometimes the tar balls were found in soft or melted condition due to heat and get mixed with sand and form large lumps(see figures 1-4).

Table II. Details of tar ball deposition with associated extraneous material along some selected beaches.

Plece of observation	Date	Deposition				Association
		EHWS	HTM	MTM	LTM	
WEST COAST						
KARNATAKA[a]						
Maravanthe	9.8.72	-	344.8	10.6	-	*Rhizophora* fruits, polychaete tubes and plastic beads.
Honavar	9.8.72	-	18.3	1.9	2.2	*Rhizophora* fruits and polychaete tubes
GOA[b]						
Arambol	31.5.73	93.2	-	-	-	Isolated, fresh and soft lumps
Sinquerim	23.6.73	4480.0	-	-	-	
MAHARASHTRA						
Deogarh	22.7.72	-	758.8	128.5	-	*Physalia* and *Rhizophora* fruits.
Ratnagiri	20.7.72	-	247.7	28.5	-	Fresh deposition. *Physalia*, *Lanthina*, *Rhizophora*, poly chaete tubes and plastic beads.
EAST COAST						
TAMIL NADU						
Mandapam	7.9.72	-	5.9	-	-	Stray deposits mainly found at HTM.
Vedaranyam	11.9.72	120.1	138.7	-	-	Old deposition at HTM. Some unidentified hard black pieces were also collected.
ANDHRA PRADESH						
Mypaud	17.9.72	-	6.2	-	-	--
Ramayapattinam	17.9.72	-	75.5	-	-	Old stray deposition at HTM.

[a] See Figure 3.
[b] See Figure 2.

The polychaete tubes, and <u>Rhizophora</u> fruits which are associated with tar indicate that its origin is in the near shore areas. The deposition also appears to be influenced by estuaries. Along the sheltered beaches, the density of tar deposition was less.

It appears that tar balls come from the oil wastes and ship spillage discharged by the ocean going vessels (2). The degraded products of oil float for sometime or may sink (3). With the approach of monsoon conditions and due to changes in coastal circulation pattern and wind direction they are washed ashore.

The above observations indicate that at some selected points along the Indian coast it is important to start a project of monitoring oil pollution.

Sampling of tar balls should be done from coastal stations, oceanic islands and by research vessels and fishing trawlers from different parts of the ocean so as to obtain the distribution of tar balls at the sea surface. Then it would be important to study the influence of currents, waves and wind pattern which are largely responsible for bringing the tar balls ashore.

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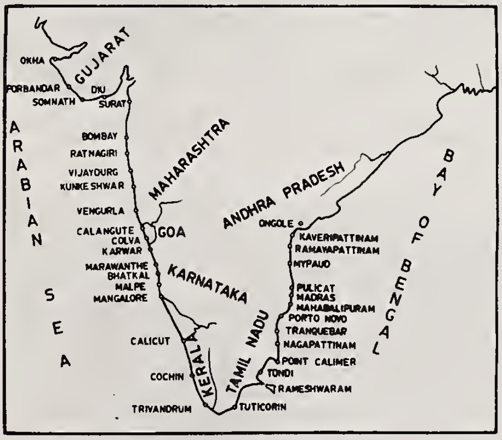
Key words: Indian beaches, Oil pollution, Quantitative study, Season, Source, Tar balls, Tide levels.

Figure 1.



Area surveyed for oil deposition along the Indian coasts during the year 1970-73.

Figure 2.

Sinquerim beach, Goa: Tar deposition at different tide levels during 1973.

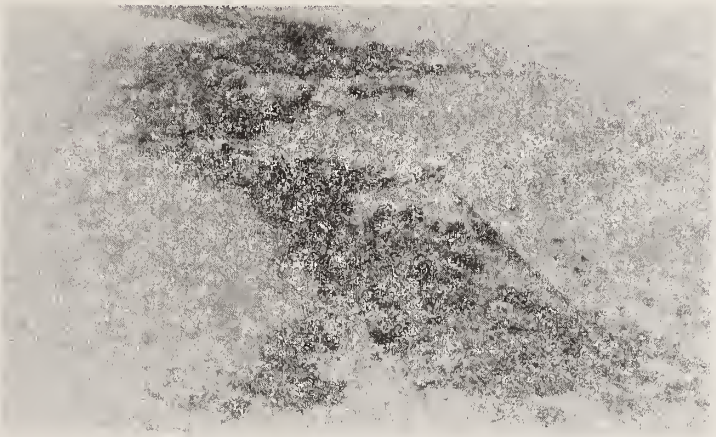
Candolim beach, Goa: Tar balls in the process of deposition during July 1973.

Sinquerim beach, Goa: Tar ball deposition at high tide level, during July 1973.

Figure 3.

Maravanthe beach, Karnataka State: Tar ball deposition during July 1973.

Figure 4.



Calicut beach, Kerala State: Tar ball deposition during 1973.

TOPICAL SESSION II.

Oil in Water: Sampling and Analytical Methods

NBS Spec. Publ. 409, Marine Pollution Monitoring (Petroleum), Proceedings of a Symposium and Workshop held at NBS, Gaithersburg, Maryland, May 13-17, 1974 (Issued December 1974).

SAMPLING ERRORS IN THE QUANTITATION OF PETROLEUM IN BOSTON HARBOR WATER

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The petroleum content of many effluents which are discharged into the environment (tanker ballast water and refinery waste water, for example) is limited by state or federal regulations. The enforcement of these regulations depends on the existence of reliable analytical methods for determining oil-in-water concentration. Many such methods are available: they make use of gravimetry [1]; volumetry [2]; infrared [3-6], ultraviolet [7] and fluorescence [7] spectrophotometry; and gas chromatography [4,8,9]. Among these techniques, the infrared spectrophotometric method seems to be the most popular [5]. Despite its widespread use, however, there is no data available on its reliability in practice. Therefore, the precision and accuracy of this method have been studied using the Boston Inner Harbor as the test case and using two techniques of oil preconcentration; namely, carbon tetrachloride extraction [1] and polyurethane foam adsorption [10].

<u>Carbon Tetrachloride Extraction</u>. The water samples (1 liter each)were obtained by submerging an open glass sample bottle upright to the desired depth and allowing it to fill. These bottles were then sealed with aluminum foil held secure with a screw cap. All samples were preserved with 3 ml of concentrated sulfuric acid, refrigerated, and extracted within 30 hours after being obtained. Once in the laboratory, the sample was poured into a 2l. separatory funnel and 30 ml of carbon tetrachloride was used to wash the bottle from which the sample was removed. This same carbon tetrachloride was then used to extract the water sample. After 30 sec agitation and a 3 min settling period, the non-aqueous phase was drained through afunnel containing about 30g of anhydrous sodium sulfate over a glass wool plug and collected in a 100 ml volumetric flask. This rinsing and extraction procedure was repeated twice more. The sodum sulfate was rinsed with 5 ml of carbon tetrachloride which was added to the extracts and the volumetric flask was made up to 100.0 ml.

Infrared spectra were taken of these extracts in a 10.0 mm cell with NaCl windows. Solutions were transferred via a pasteur pipette, washing the cell twice with the solution to be observed before filling. Spectra were scanned from 3400 cm^{-1} to 2500 cm^{-1} using 5 to 10 times expansion of the percent transmission scale. The C-H stretching band at 2930 cm^{-1} was used for analysis. The absorptivity at this wavelength as calibrated with a motor oil (SAE 30 weight) was 3.39 $l\ g^{-1}cm^{-1}$. A typical procedural blank corresponded to an oil concentration of less than 0.010 mg/l.

Samples used in the recovery study were produced by adding known weights of the motor oil to sample bottles which were then filled about 1/4 full with distilled water and shaken. Concentrated sulfuric acid (2.5 ml) was added, the bottles filled with distilled water and immediately processed as described above.

<u>Polyurethane Foam Adsorbtion</u>. The foam adsorbtion method was implimented as described previously [10]. In brief, 10 to 50 liters of sea water were passed through a foam disk (8 cm diameter, 4 cm thick, 100 pores/in) and then the retained oil was extracted in Soxhlet apparatus with carbon tetrachloride. This extract was measured as described above. It was found necessary to clean new disks by Soxhlet extraction with carbon tetrachloride for four to six hours in order to reduce blank analyses to acceptable levels. It has previously been shown that recoveries of known concentrations of oil were greater than 85% for those concentrations above 5 mg/l [10]; lower concentrations were not studied [10].

<u>Results and Discussion</u>. In order to determine the performance of the carbon tetrachloride extraction method itself devoid of any sampling errors, a recovery study was carried out. Solutions of oil in water of known concentrations were prepared as described above and analyzed. These results are shown in Table I; excluding the one point of lowest concentration, the average recovery is 101% and the average error is 13%. Therefore, the method itself seems quite reliable since

Table I. Recovery Study Data

Oil Added	Oil Measured	% Recovery
6.12 mg/l	5.96 mg/l	97
3.43	3.66	107
2.26	3.10	137
1.85	1.89	102
1.42	1.41	99
1.26	1.14	91
0.74	0.65	88
0.57	0.46	81
0.46	0.57	124
0.34	0.24	71
0.22	0.22	100
0.17	0.16	94
0.14	0.13	93
0.08	0.11	139
0.01	0.03	---

the quantity of oil in the sample bottle can be determined with relative standard deviation of less than 15% for concentrations exceeding about 0.05 mg/l.

Samples were taken in replicate from Boston Inner Harbor at various stations at two depths: surface (0-5 cm) and subsurface (25-35 cm). All replicate samples at a given station and depth were taken simultaneously (± 30 sec) and from within an area of about one square meter. The analyses of these samples is shown in Table II.

Table II. Oil Concentration in Boston Harbor Water (mg/l)

Station number	Surface (0-5 cm)	Subsurface (25-35 cm)
1A	0.631	0.029
	1.54	<0.025
	0.407	<0.025
	0.708	0.394
	0.793	0.698
ave.	0.816	0.234
rel.s.d. [a]	53%	130%
confid.lim. [b]	0.4-1.2	0.0-0.5
2A	0.213	0.143
	0.030	0.089
	0.197	0.308
	0.320	0.072
ave.	0.190	0.153
rel.s.d.	63%	72%
confid.lim.	0.1-0.3	0.0-0.3
1C	0.546	0.074
	0.256	0.254
	0.306	0.096
	<0.025	0.034
ave.	0.283	0.114
rel.s.d.	75%	84%
confid.lim.	0.1-0.4	0.0-0.4
2C	0.153	0.077
	0.296	0.060
	0.368	0.269
	0.138	0.366
ave.	0.239	0.193
rel.s.d.	46%	78%
confid.lim.	0.1-0.4	0.0-0.4

Notes:
a. relative standard deviation of a single measurement
b. 90% confidence limits of mean
c. average relative standard deviation = 75%

The relative standard deviations for each set of replicates ranges from 46% to 130% with the average being 75%; this variability is far in excess of the varibiility of the analytical procedure itself (15%). This error must, therefore, be associated with sampling from a heterogeneous system such as oil in water.

A model of this oil in water system will serve to quantitate the natural variability which is necessary to produce this observed variability in the measurement (75%). The model assumes that the oil is coated on, or in some way associated with, the particulate matter in the Harbor water and that there are N of these particles per liter of water. If each particle has X milligrams of oil associated with it, the measured oil concentration C is given by

$$C = NX \tag{1}$$

and therefore the relative standard deviation S_C of C is approximately

$$S_C = (S_N^2 + S_X^2 + S_A^2)^{1/2} \tag{2}$$

where S_N, S_X and S_A are the relative standard deviations of the number of particles N, of the weight per particle X, and of the analytical procedure, respectively. If it is assumed that $S_N = S_X$, $S_C = 75\%$, and $S_A = 15\%$; then $S_N = S_X = 52\%$. In other words, if the density of particles (N) and the oil per particle (X) have a relative standard deviation of 52%, the measured concentration would have a relative standard deviation of 75%. This magnitude of variability in the natural system seems quite modest considering the polluted state of Boston Inner Harbor.

A detailed examination of Table II shows that only the 1A surface sample differs significantly from all the others. This sample was taken in an area located close to an oil unloading complex and on a day when a light to heavy sheen was observed on the water. With this one exception, the ambient oil concentration observed in this study was less than 0.5 mg/l. Furthermore, the lack of significant differences in Table II, particularly between corresponding surface and subsurface samples and between different locations, indicates that the sampling error effectively obscures the expected variation in oil concentration due to tides, currents, and depth. Thus one can pool all 34 data in Table II to obtain an average oil concentration in Boston Harbor during this study (July and August 1973). This average is 0.292 mg/l and the stanard deviation of the mean is 0.053 mg/l; thus with 95% confidence the oil concentration is 0.188 to 0.396 mg/l.

Comparative data for the extraction and foam adsorption preconcentration methods are given in Table III. In all cases the oil concentration resulting from the foam technique is the lower of the two values; in fact, it is low by a factor of five on the average. Although there are sampling errors associated with both techniques (which may well account for the scatter in the ratios), it is clear that the foam technique has a much lower collection efficiency than liquid-liquid extraction and is, therefore, a less useful procedure.

Table III. Comparison of oil concentrations determined using different preconcentration techniques (surface samples only).

Station number	CCl_4 Extraction	Foam Adsorbtion	Ratio
1B	84.1 mg/l	7.2 mg/l	11.7
2B	0.10	0.08	1.25
3B	0.21	0.03	7.0
1C	0.283[a]	0.19	1.5
2C	0.239[a]	0.07	3.4
		ave.	5.0

a) average of four values (see Table II)

Conclusions. There are, in principle, two major ways of reducing the large sampling error that was observed; namely, replicate samples and larger sample sizes. These two methods do not, however, have an equal effect on the overall precision (S_C). To demonstrate this effect, the following assumption is made: the number of particles per unit volume (N) is quite small and, thus, follows a Poisson distribution. If this is the case, the relative standard deviation of N is given by

$$S_N = \frac{100\sqrt{N}}{N} . \tag{3}$$

Therefore, the overall precision resulting from n replicate analyses is

$$S'_c = \left(\frac{10^4}{nN} + \frac{S_x^2 + S_A^2}{n}\right)^{1/2} . \tag{4}$$

One can now see what the effects of replication and sample size are. In the extreme, as n becomes infinitely large S'_c approaches zero. However, as sample size (and thus N) becomes infinitely large, S'_c approaches $[(S_x^2 + S_A^2)/n]^{1/2}$ which, if $S_x = 52\%$ and $S_A = 15\%$, is 54% for a single analysis. In other words, the overall precision is limited by the analytical error (S_A) and the variability of the weight of oil on the individual particles (S_x) and, therefore, increasing sample size will not be worthwhile if these values are at all high. Increasing the number of replicates, however, directly improves the overall precision by a factor of $n^{1/2}$ over that of a single analysis.

An example may make these concepts more concrete. For the data reported above S_c =75%, n =1 we see that N = 3.71 l^{-1}. Increasing the sample size to one gallon (3.785 l.) and analyzing three samples gives an increased precision of 35%. Keeping the sample size at one liter but analyzing four samples gives $S'_c = 75\%/\sqrt{4} = 37\%$. Clearly this latter case is preferred from a practical point of view since less total water needs to be transported.

Finally, a few words on the magnitude of the sampling error as a function of oil concentration should be said. At high oil abundances most of the oil is present on the water as a layer of varying thickness and relatively little oil is dispersed. Obviously, the measurement of most interest is the thickness of the surface oil layer not the concentration of the dispersed oil beneath it. In these circumstances, therefore, one would not make an oil concentration measurement as described here. At the other extreme, very low concentrations of oil will actually be in solution and the sampling errors described here will not exist [5]. The sampling problem becomes much more severe however at intermediate concentration (∿0.025 to ∿25 mg/l) and it is this oil concentration regime which requires attention to the magnitude of the sampling error.

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Key Words: Petroleum-in-water analysis; Boston Inner Harbor; Sampling errors; Infrared quantitation of petroleum.

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HYDROCARBON CONCENTRATIONS IN SEAWATER ALONG THE HALIFAX-BERMUDA SECTION: LESSONS LEARNED REGARDING SAMPLING AND SOME RESULTS

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During the last three years, we have been attempting to measure the extent of petroleum hydrocarbon contamination in seawater off eastern Canada. Most of our attention has been directed to an oceanic section between Halifax and Bermuda (Fig. 1). During nine cruises, we have tested different sampling and analytical procedures and have developed methods which we believe provide fairly accurate data of hydrocarbon concentrations in seawater. We have been using fluorescence spectroscopy to estimate aromatic hydrocarbons and gas chromatography to measure paraffic hydrocarbons. In light of the purposes of this workshop and symposium, I shall restrict my presentation to our work using fluorescence spectroscopy, stressing the attention that must be given to sampling procedures.

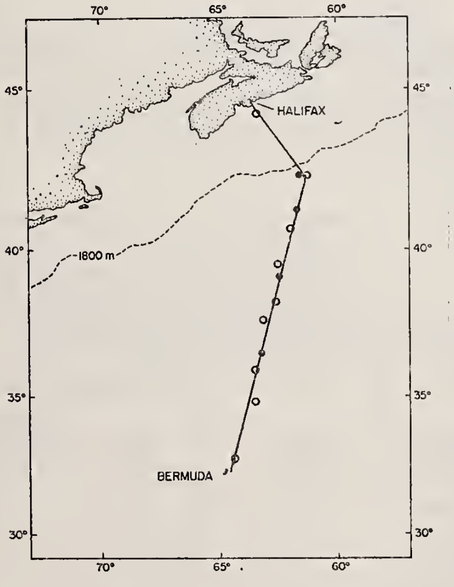

Figure 1. Location of the Halifax-Bermuda section

Sampling Equipment

Surface film samples are collected with a device we call a slurp bottle (modelled after a sampler originally described by Goering and Menzel [1]). A gallon glass bottle is fitted with a one-hole stopper (made of non-fluorescing and hexane-resistant material) through which is inserted a piece of glass tube. A 30 cm length of flexible (but inert to hexane) tubing which is fitted with corks along its length so that it will float at the sea surface is attached to the outer end of the tube. A vacuum of 65 cm Hg is drawn and the sampler is thrown overboard away from the ship just as it is stopping on station (before the surface layer can be contaminated). About 100-300 ml of seawater is drawn into the bottle from the upper 5 mm through the tubing in about 15 sec. After filling, the sampler is retrieved using an attached line.

Shallow samples (1 to 5 m) are collected in glass bottles of 2.28l volume. These are placed in a weighted metal frame attached to a line and tossed overboard away from the ship immediately after slurp samples are collected. A float attached to the line suspends the glass bottle a given distance below the seasurface, the inside of the bottle never comes into contact with the surface film.

For deeper samples, the best samplers (but not perfect for reasons discussed later) we have located are teflon-lined stainless steel Knudson bottles of 1.25 l volume. Before using, all rubber and leather gaskets must be replaced with teflon and the entire bottle must be thoroughly cleaned inside and out with methylene chloride (or similar solvent) to remove any traces of oil and grease (even after doing this before our most recent cruise, it wasn't until the fifteenth station that the bottles appeared to be truly "clean"). These bottles are lowered <u>open</u> on a hydrographic wire.

In the earlier stages of our work, we used 12-l and 30-l Niskin bottles (closed with rubber tubing) to collect water samples. To our surprise and grief, we recently learned that the data obtained using the Niskin bottles are inaccurate. By conducting a number of laboratory and field experiments, we have observed that fluorescing material in seawater (both raw and spiked with crude oil) is quickly adsorbed to the inner surface of Niskin bottles. This process is reversible and these compounds can accumulate and be released to subsequent water samples collected if the bottles are not washed with solvent after each use. In our earlier work, we washed the bottles only with fresh water and isopropanol before and after each cruise, a procedure that did not remove the adsorbed material. As demonstrated in a later section, this adsorbed fluorescing material was being added to our samples causing the resultant concentrations to be erroneously high.

Our experience indicates that all water samplers must be rinsed with solvent (hexane or methylene chloride depending upon the sampler) after each use to recover any adsorbed material lost from the enclosed water sample. Also, the entire contents of a sampler must be extracted, so samplers must range from about 1 to 5 l in volume.

Extraction and Preparation of Blanks

Since the volume of slurp samples is small (generally 100-300 ml), they can conveniently be extracted with hexane. After the water is transferred to a 500-ml glass separatory funnel, 30 ml of hexane is added to the slurp bottle through the inlet tubing and swirled around making sure that it comes into contact with the entire inner surface of the slurp bottle. This hexane is then added to the water sample and the extraction performed.

Water collected in glass and Knudsen bottles is transferred to 4-l glass separatory funnels. Bottles are then thoroughly rinsed twice with 40 ml of methylene chloride which is then added to the water and the extractions performed.

We use methylene chloride in place of carbon tetrachloride (used by Levy [2]) because of its lower toxicity and lower boiling point (40.1°C compared to 76.8°C). Comparison of the two solvents indicates that using carbon tetrachloride causes about half the fluorescing material in seawater (both raw and spiked with fresh crude oil) to be lost, most probably during the evaporation step [3].

Frequent blanks must be prepared by rinsing samplers with solvent (slurps are first evacuated) and then passing the solvent through the separatory funnels; the same procedure as with samples but no water is present. Merely setting aside a bit of solvent is not sufficient for a blank.

Laboratory Analysis

Extracts are returned to the laboratory in glass vials or bottles sealed with aluminum foil-lined caps. Extracts should be kept dark to avoid photochemical reactions (especially with methylene chloride extracts). Hexane extracts are analyzed directly; methylene chloride extracts are evaporated in a rotary evaporator under slight vacuum and the residue taken up in hexane. Hexane extracts are analyzed by fluorescence spectroscopy [3] using the same instrument and similar operating conditions as Levy [2]. The instrument is calibrated daily with Venezuelan crude oil. For convenience, the data are reported in units of crude oil equivalents. It must be remembered that the observed fluorescence may not be due to petroleum hydrocarbons and the actual concentration of any naturally-occurring fluorescing material could be much different than the crude oil equivalent concentrations.

Results

The results obtained using these procedures on our most recent cruise are presented in Table 1. Concentrations are greatest in the surface film and drop quickly with depth in the upper 5 meters. There were no apparent

Table I. Concentrations of hydrocarbons (crude oil equivalents) detected in seawater along the Halifax-Bermuda section in April 1974 as measured by fluorescence spectroscopy.

		μg/l		
Sampler	Depth	n	Mean	Standard Deviation
Slurps	1-5mm	53	9.28	18.38
Glass bottle	1m	23	0.56	0.58
Glass bottle	5m	24	0.37	0.42
Knudsen bottles	10-1000m	50	0.79	0.69
Knudsen bottles[1]	10-1000m	15	0.81	0.81

---

[1] lowered and retrieved open, no water collected.

regional differences in concentration at any depth. Concentrations at 10 m and deeper (collected with Knudsen bottles) are greater than at 1 and 5 m (collected with glass bottles). This appears to be an artifact for when Knudsen bottles are lowered and retrieved open similar concentrations are obtained (Table 1). Therefore we conclude that there is little if any fluorescing material in seawater deeper than 10 m along the Halifax-Bermuda section. The measurable fluorescence obtained from Knudsen bottle samples must represent 1) underestimating blank values, 2) material emanating from the hydrographic wire, or 3) material picked up by the Knudsen bottle as it is lowered open through the surface film. The greater concentrations observed by us earlier using Niskin bottles (Table 2) are apparently the result of contamination.

Table II. Erroneous hydrocarbon concentrations (crude oil equivalents) observed along the Halifax-Bermuda section when samples were collected with Niskin bottles (October 1971-October 1973)

Depth (m)	n	µg/l Mean	µg/l Standard Deviation
1-10	307	2.75	2.2
11-100	497	2.60	2.3
101-1000	159	2.36	2.0
>1001	64	2.12	2.2

Conclusions

1. Petroleum hydrocarbon contamination in seawater along the Halifax-Bermuda section appears limited to the upper few meters. Most is contained in the surface film. The large standard deviation indicates that the distribution is quite spotty.
2. The entire volume of seawater collected in a sampler must be extracted and the sampler must be rinsed with solvent after each use to recover adsorbed material.
3. The inner surface of samplers being lowered to sub-surface water must not come into contact with the surface film.
4. Deep water samples for hydrocarbon analysis must be collected with a device like the organic free water sampler designed by Dr. Max Blumer and manufactured by Benthos, Inc.
5. A monitoring program such as is being planned is of no value unless sampling and analytical procedures are thoroughly tested, discussed and cross-checked before it begins. Too often we let our desire for data blind us from faults in our methods.

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Keywords: Oil pollution, petroleum or aromatic hydrocarbons in seawater, water sampling, fluorescing material in seawater, fluorescence spectroscopy.

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DETERMINATION OF AROMATIC HYDROCARBONS IN SEA WATER USING AN ELECTROLYTIC STRIPPING CELL

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This paper describes a head-space method for determining aromatic hydrocarbons in sea water. The hydrocarbons are stripped from sea water, under equilibrium conditions, by very small bubbles of hydrogen gas generated electrolytically from a gold electrode located at the bottom of a cylindrically shaped cell. The hydrocarbon concentration in the sea water is determined from the volume of the sea water and the hydrocarbon concentration in the head-space after a measured volume of hydrogen has bubbled through the stripping cell.

Figure 1 shows a drawing of a typical stripping cell. The large compartment (A) has a volume of 1000 ml. The small compartment (B) has a volume of approximately 200 ml. The two compartments are connected by a 35-mm OD glass tube with a 30-mm ID coarse porosity glass frit (C) at one end. On the small compartment side of the frit is a silicic acid plug. The two gold electrodes (1-mm OD wire) were held in each compartment by means of a septum located in a 1/4 x 1/4-inch union fitting. The electrode (D) in the large compartment has a spiral configuration to provide a large surface area. The hydrogen headspace was sampled by a gas sampling valve thermostated at 100°C. The chromatographic column was a 15.24 x 0.508 mm ID. SCOT prepared with finely ground diatomaceous earth plus fused silica support and coated with a mixture of m-bis(m-phenoxyphenoxy) benzene and Apiezon L.

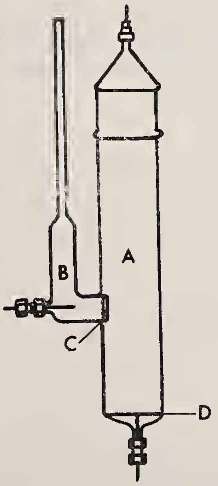

Figure 1. Electrolytic Stripping Cell.

A constant current device provides the electrical current to the stripping cell. The volume of hydrogen, V, bubbled through the large compartment is calculated from the equation:

$$V = it/F \cdot 11{,}207 \cdot T_c/273.15 \qquad (1)$$

where i is the current, t the time in seconds, F the Faraday constant and T_c the temperature of the stripping cell.

Theory

Consider a measured volume of sea water in a cylindrically shaped vessel containing a gold electrode at the bottom of the cell. Connected to this vessel by means of a glass fritted disc is a smaller cylindrically shaped vessel containing a gold electrode and an aqueous solution of sulfuric acid. When an electrical current with the appropriate polarity is allowed to flow through the cell, hydrogen, in the form of very small bubbles, is evolved at the gold electrode in the large vessel while oxygen is evolved from the gold electrode in the small vessel. The dissolved hydrocarbons in the sea water come to equilibrium with the hydrogen bubbles and their concentration is measured by gas chromatography.

If one assumes that the concentration of a particular hydrocarbon in the hydrogen leaving the cell is proportional to its concentration in the sea water one then has the relation:

$$C_i(V) = S_i(V)/K_i \qquad (2)$$

where $C_i(V)$ is the hydrocarbon concentration in the hydrogen, $S_i(V)$ is its concentration in the sea water when volume, V, of hydrogen has passed through the sea water, and $1/K_i$ is the proportionality factor. If there is equilibrium, K will be equal to the partition coefficient. One can show that the ratio of $C_i(V)$ to its value, $C_i(0)$, at zero hydrogen volume is given by the expression:

$$\ln(C_i(V) / C_i(0) = \ln(S_i(V)/S_i(0)) \qquad (3)$$

$$= -V/KV_L$$

where V_L is the volume of the sea water and $S_i(0)$ is the concentration of a particular hydrocarbon in the original sea water.

The fraction of the total amount of a particular hydrocarbon, $S_i(V)/S_i(0)$, extracted by a given V/V_L of hydrogen depends upon the magnitude of K_i. For the case of gasoline dissolved in sea water at 80°C we observed that 95% of the aliphatic and olefinic and only 0.4% of the aromatic hydrocarbons are extracted when V/V_L is equal to 0.046. Thus the aliphatic and olefinic hydrocarbons are quickly stripped from the cell for low values of V/V_L leaving a large fraction of the aromatic hydrocarbons in solution. After the aliphatic and olefinic hydrocarbons are stripped out of solution, the concentration of the aromatic hydrocarbons can be measured for different V values. From the plots of $\ln C_i(V)$ vs. V/V_L the slope $1/K_i$ and intercept $\ln C_i(0)$ is obtained for each hydrocarbon. The aromatic hydrocarbon concentrations in the original sea water can then be calculated from the expression $S_i(0) = K_i C_i(0)$. Once the K's for the aromatic hydrocarbons are known, $S_i(0)$ may be determined from the expression:

$$S_i(0) = C_i(V) K_i \exp (V/V_L K_i). \qquad (4)$$

In this case only one value for $C_i(V)$ is required.

For the case of gasoline, we added 0.05 ppm toluene-d_8 as an internal standard to 1000 ml of a dilute aqueous solution of un-leaded gasoline. The diluted extract was poured into a 1000 ml stripping cell located in a constant temperature water bath. The temperature of the water bath was raised to 80°C and 0.3 amperes of current were passed through the cell. The upper chromatogram shown in Figure 2 was obtained by sampling 1 ml of the head-space after 30 ml of hydrogen had bubbled through the stripping cell. This chromatogram shows the large number of aliphatic and olefinic hydrocarbon peaks that are eluted. At the same time the early aromatic hydrocarbon peaks are also eluted. The lower chromatogram in Figure 2 was obtained after 46 ml ($V/V_L = 0.046$) of hydrogen had bubbled through the cell. All the aliphatic and olefinic hydrocarbon peaks are absent from this chromatogram. The head-space was sampled three other times at different V values and the peak areas were measured with an electronic integrator. From the log $C_i(V)$ vs. V/V_L plots the slopes, $1/K_i$'s, and intercepts, $C_i(0)$'s, were determined. The amount of each aromatic hydrocarbon in the original solution was calculated from equation 4.

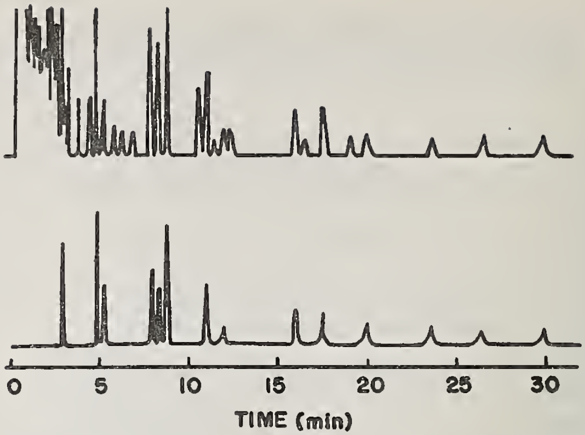

Figure 2. Chromatograms of the head-space gas showing the aliphatic, olefinic, and the early aromatic hydrocarbons eluted after 30 ml of H_2 gas bubbled through the cell (upper) and the aromatic hydrocarbons eluted after 46 ml of H_2 gas bubbled through the cell (lower).

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Key Words: Head-space; Electrolytic stripping cell; Aromatic hydrocarbons; Partition coefficient; Sea water.

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DETERMINATION OF AROMATIC AND TOTAL HYDROCARBON CONTENT IN SUBMICROGRAM AND MICROGRAM QUANTITIES IN AQUEOUS SYSTEMS BY MEANS OF HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

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In order to determine the hydrocarbon concentration in small water samples (under 51) rapidly and fairly simply, two separate but related methods were developed [1, 2]. Both are based upon the use of high performance liquid chromatography. They are more sensitive than the IR methods, which tend to have a maximum sensitivity of 0.05 mg [3], and they are probably more specific than UV or fluorescence methods used without column chromatography [4]. Their main advantage over GLC lies in the fact that they are simpler and more rapid for the obtaining of quantitative results [5].

For the extraction of hydrocarbon material from the aqeous system, a liquid extraction method is used, since it is the simplest and most direct method. It also has the advantage that blanks can easily be prepared. The solvent used to extract the hydrocarbons is 1,2,2-trichlorotrifluoroethane (TCF). It was found to have several advantages. It is a virtually non-polar compound that is not a hydrocarbon. It is heavier than water, which enables it to be removed simply with a pipette from the bottom of the extracting vessel, and it boils at 47.6°C, enabling it to be concentrated quite readily. In addition, it is transparant to UV light at 254 nm.

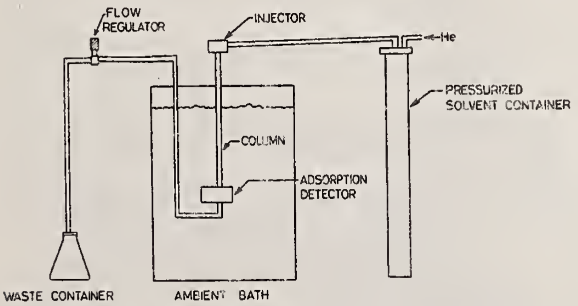

Figure 1. Layout of the high performance liquid chromatography system used to detect the total hydrocarbon content. The tubing has an O.D. of 1/8 in. and the ambient bath a volume of about 12 ℓ.

Ten ml of TCF are added to each liter of water to be extracted and shaken for about 5 min. and then allowed to stand for 10 min. to permit the phases to separate. The extract is then removed with a pipette and concentrated down to about 1 ml or so under vacuum. Afterwards it is placed in a special concentrating tube, which is simply a small test-tube that has part of a sealed pipette with 10 μl gradiations fused on it so that the amount of extract that remains after concentration can be read with an accuracy of 5 μl. This final concentrating phase is done with a stream of molecular sieve cleaned nitrogen until the extract was reduced to 100 μl. The concentrating procedure is by far the most time consuming and the most prone to contamination, making it absolutely essential that blanks be run.

The apparatus used to determine the "total" hydrocarbon content is shown in figure 1. The flow calorimeter, which is used to detect the hydrocarbons is shown in figure 2.

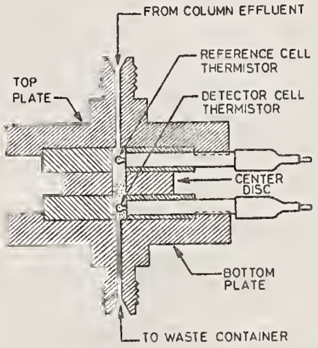

Figure 2. Diagram of the flow calorimeter used. It is an adsorption detector, with the detector cell thermistor embedded in a material that is capable of adsorbing hydrocarbons.

It roughly operates on the following principle. Two thermistors are in the solvent stream, and one of them is embedded in a substance that is capable of adsorbing hydrocarbons. As long as there is no material coming off the column, the circuit is balanced. However, when material comes off the column, it is adsorbed on the adsorbent surrounding one of the thermistors. The heat of adsorption that results, also produces a change in the resistance of the thermistor, which then leads to an imbalance in the circuit and a peak on a recorder. This process is reversible and a peak in the opposite direction to the first one results right afterwards as the material is being desorbed. The adsorbent that is used is porous glass beads with a pore size between 3.0 and 4.5 nm.

The column that is used in the system to separate non-hydrocarbons from the hydrocarbons has an I.D. of 1.8 mm and is 5 cm long. It is filled with 10% deactivated silica gel. The resulting system was found not to produce any response even with such slightly polar substances as stearic acid n-decylester or methyl palmitate. The saturated hydrocarbons were all found to have a response between 76 to 110% of n-nonadecane, which was used as the standard throughout. Unsaturation decreased the response per unit weight. This decrease was minor among the mono-unsaturated compounds, but quite strong among the poly-unsaturated alkenes such as carotene and squalene. The former produced no response, and the latter had a response that was 32% of nonadecane's. This means that this method will tend to underestimate the hydrocarbon content when there is a large proportion of unsaturated compounds present. If one assumes that 50% of the hydrocarbons present are unsaturated and that the unsaturated hydrocarbons have, on average, a response per unit weight that is 50% of that of nonadecane, the value determined will be 25% too low. This is naturally only a very rough estimate, but even under these extreme conditions, one can see that the underestimation is still at a tolerable level, when one considers the complexity of the problem of measuring hydrocarbons in the aquatic environment.

Aromatic hydrocarbons will also be underestimated. Naphthalene, for example, has a response that is only 29% of that of nonadecane. However, their contribution to the total hydrocarbon content in non-stagnant and not severely polluted water is very low [6], quite likely well under 10% [7].

The smallest amount that can readily be detected is 2.0 ± 1.7 μg, based on nonadecane. The high standard deviation is due to poor reproducibility in both the extracting and the concentrating phase.

For the determination of the aromatic hydrocarbons, the same extracting and concentrating procedure is used as above. The apparatus is somewhat different in that a UV detector, which measures absorbance at 254 nm, replaces the flow calorimeter and the ambient bath is not needed. A longer column (10 cm) with more active (2% deactivated) silica gel is also used, since aromatic hydrocarbons are somewhat polar and more care must be taken to assure their separation from other weakly polar compounds.

The chief disadvantage in the use of a UV detector lies in the fact that the response per unit weight varies enormously from compound to compound. As a result all values can only be given relative to a standard and will vary greatly depending upon the standard selected. A similar procedure is often used in measuring the proteins in aquous systems where albumin is usually the standard. It was decided that phenanthrene was probably the best choice here, because of its "intermediate" size among the possible aromatic hydrocarbons. Benzene is not suitable, since one can assume that most of the benzene compounds are lost during the concentrating, because of their relatively low boiling point. If naphthalene is used as a standard, all the values found will be larger by a factor of about 10, since naphthalene absorbs at 254 nm only about 0.1 times as well as phenanthrene. One indication, however, that phenanthrene is a suitable choice is that almost all the samples that were measured in the sea by the author had a retention time that was intermediate between that of phenanthrene and naphthalene, tending to indicate that the majority of the aromatic compounds were substituted 3 ring ones. Nevertheless, caution must be used in interpreting the quantitative data obtained until a final definitive standard has been selected.

Due to the extreme sensitivity of the UV detector, only 20 μl of the concentrated extract needs to be injected. The smallest amount of material, based upon phenanthrene, that could readily be detected was 4 ± 10 ng. Again, the high errors in the extracting and concentrating procedure are responsible for the large standard deviation. In order to minimize its effect, sample sizes should be as large as possible. Both these methods have been successfully used at sea [7].

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DETERMINATION OF C_1-C_{10} HYDROCARBONS IN WATER

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Several fields require the measurement of widely varying concentrations of hydrocarbons dissolved in water. These fields include environmental studies, petroleum exploration, and biochemical research, among others. The method reported here is based on successive gas chromatographic analyses after repeated equilibrations of a hydrocarbon-free gas with an aqueous sample containing dissolved hydrocarbons. All classes of hydrocarbons having up to 11 carbon atoms in the molecule can be determined.

EXPERIMENTAL METHOD

Sample Collection and Preservation

It is desirable, if possible, to analyze the aqueous sample for hydrocarbons at the time of its collection. In many cases, however, this is not possible. A sample, therefore, should be collected in a glass container, tightly sealed with a minimum gas space over the water, and having only teflon in contact with the water. A bactericide must be added to the water prior to sealing to prevent biodegradation of the hydrocarbons.

Laboratory Measurements

Typically, a 50-ml glass hypodermic syringe (with Luer-Lok fitting and an appropriate valve) is flushed several times with portions of the aqueous sample of which 25 ml is finally retained. Twenty-five ml of helium (nitrogen, air or other hydrocarbon-free gas) is added and the syringe capped. It is then vigorously shaken on a paint shaker for 3-5 minutes or approximately 20 minutes on a laboratory wrist action shaker to establish equilibrium between phases. Twenty to 23 ml of the gas phase is then flowed through the sample loop (previously flushed with helium) of the gas chromatograph, and then a measured volume, usually from 1-10 ml of the gas is introduced for analysis.

The remaining gas in the syringe is carefully discharged by moving this solution to the syringe tip, and 25 ml of fresh helium is added. The equilibration process is repeated as many times as is required for the specific application. The reader is referred to the original publication [1] for details of the method. Wasik and Brown [2] have modified the technique to permit automation and constant temperature conditions.

A plot of the log of the hydrocarbon concentration in the gas phase versus the number of equilibrations produces a straight line. From the semi-log line read any two adjacent gas phase concentrations. Divide the greater by the lesser and subtract 1. This is the distribution coefficient. Note the intercept of the line, divide it by the distribution coefficient, and one has the desired concentration in the original sample after correction for instrument response and sample size.

Partitioning of Hydrocarbons

Different classes of hydrocarbons partition differently between water and gas phases based upon their solubilities in water and their vapor pressures. Thus, the different distribution coefficients permit the separation of the various hydrocarbon types. Figure 1 graphically demonstrates the way that different classes of hydrocarbons partition. The original solution was formulated in tap water to give approximately the same peak heights for benzene, cyclohexane, and n-hexane following the first equilibration. The second equilibration resulted in a small n-hexane peak, the cyclohexane peak reduced approximately 90%, and a toluene peak reduced by

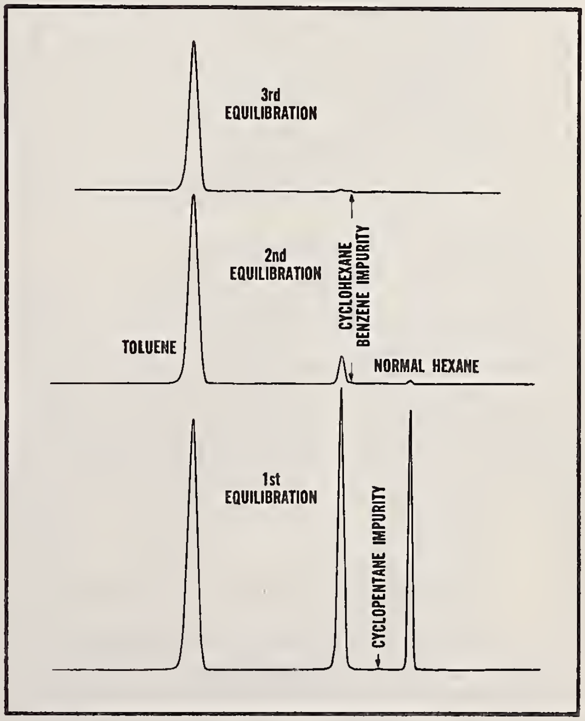

Figure 1. Partitioning of three different classes of hydrocarbons between equal volumes of tap water and helium at 25°C for successive equilibrations.

approximately 20%. The third equilibration shows no n-hexane peak, a very small cyclohexane peak, and toluene as the major hydrocarbon remaining.

Olefin and acetylene hydrocarbons would distribute between the water and gas phase with different distribution coefficients. If present in the water sample, they could be identified and measured. The percentages of total hydrocarbon in the gas phase calculated from solubilities and vapor pressures [3,4] (for equal volumes of gas and distilled water) for 1-pentene, 1,4-pentadiene, and 1-pentyne are 94, 83, and 51 respectively.

Because alkanes have low solubilities in water compared to their vapor pressures, 96+% of them partition into the gas phase when equal volumes of gas and water are equilibrated. Thus, analysis of the first equilibration is sufficient to determine alkane concentration in the water phase except for the most precise determination. If higher accuracy is required, the concentration in the gas phases of the first two equilibrations can be summed.

Cycloalkanes partition less into the gas phase than do alkanes. Figure 2 shows that after 3 equilibrations, cyclohexane had been 99.7% transferred to the gas phase.

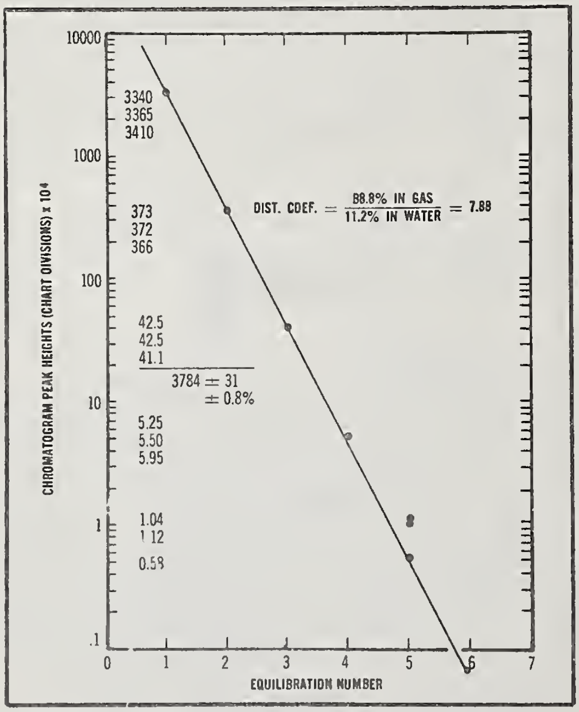

Figure 2. Partitioning of cyclohexane between equal volumes of tap water and helium at 25°C for successive equilibrations.

Aromatic hydrocarbons remain principally in the water phase when equal volumes of water and gas are equilibrated. Figure 3 shows the actual data points for repeated equilibrations of toluene with waters of varying salinity. It is apparent that unless the water is highly saline many equilibrations would be required to remove the majority of the toluene. Therefore, the most convenient method for determining the original concentration is to fit a straight line to the data points and back extrapolate.

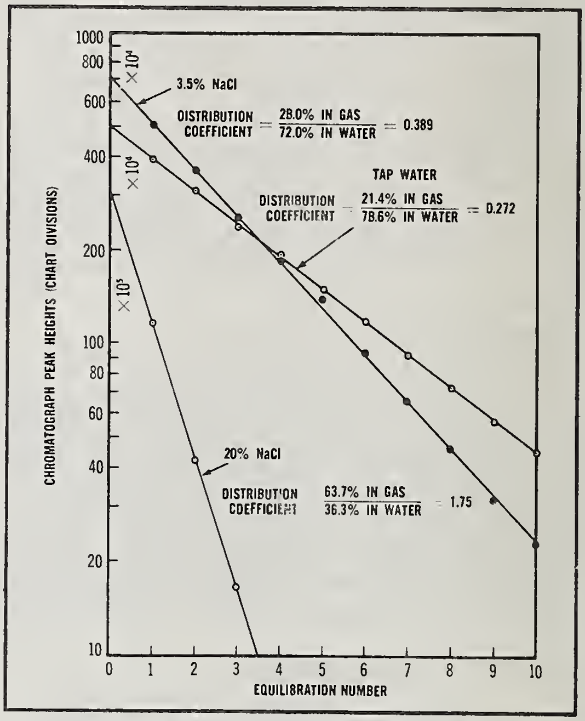

Figure 3. Partitioning of toluene between equal volumes of three salinity waters and helium at 25°C for successive equilibrations.

One of the principal advantages of this method is its ability to determine hydrocarbon concentrations accurately in solutions of varying ionic composition. It matters little whether the water is fresh, brackish, sea water, or subsurface brine.

Separation from or Identification of Non-Hydrocarbon Organic Compounds

The method gives good separation of hydrocarbons from highly water-soluble organic compounds such as alcohols, aldehydes, ethers, and acids. Because of the high water solubilities of these organic compounds, the distributions are highly favored toward the water phase, and little of them is found in the gas phase. If the water phase should contain a sufficiently high concentration of an organic compound for it to appear in the gas phase, then the gas phase concentration decreases very slowly with successive equilibrations. Such distribution coefficients, along with relative retention time, help identify unknown organic compounds.

Method Sensitivity

When we use the described procedure and introduce a 5-ml gas sample into the chromatograph, the method is capable of detecting alkane and cycloalkane hydrocarbons in water if they are present in amounts of 1-3 parts in 10^{12} parts of water by weight. Aromatic hydrocarbons, because of their lower partitioning into the gas phase, can be detected if present in concentrations of 4-12 ppt. Reasonable accuracy can be obtained if the aqueous concentrations are 20-30 times these values.

APPLICATIONS OF THE METHOD

Contaminants in Drinking Water

An actual example of the indentification of organic contaminants in a tap water sample from a city water supply is shown in figure 4.

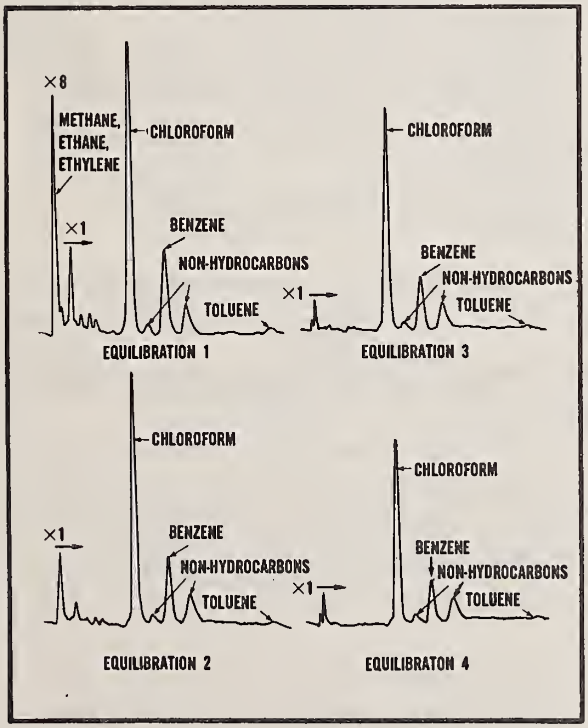

Figure 4. Organic contaminants in tap water from a city water supply.

The first peak is predominantly methane and/or other low molecular weight alkanes and olefins. The next prominant peak has the relative retention time for n-hexane, but the additional equilibrations gave a distribution coefficient that duplicates that for chloroform (as calculated from solubility and vapor pressure data). Confirmation was made by adding chloroform to water and analyzing. Benzene and toluene were identified also by relative retention times and distribution coefficients.

This drinking water supply was monitored almost daily for an 18-month period and the concentrations observed are representative of that time period. The concentrations are: chloroform 8-10 ppb, benzene 2-3 ppb, and toluene 0.2 ppb. Recently Novák et al [5] report benzene and chloroform in pure drinking water in Czechoslovakia, but concluded that the contamination of the drinking water with these compounds took place during manipulation in the laboratory. The results reported in figure 4 were observed at the same time sea water samples were being analyzed; the latter contained only methane. Thus, laboratory contamination did not contribute to the compounds shown in figure 4, and chloroform and benzene may have been in the water reported by Novák and coworkers.

Environmental Surveys

Another advantage of the gas equilibration technique is that no sample manipulation or sample preparation is required. The sample can be analyzed immediately upon collection. This was done in a study of water samples in the Cook Inlet [6]. A gas chromatograph was placed aboard the University of Alaska, Institute of Marine Science's research vessel. Water samples were collected from near surface, mid-depth, and near bottom from some 60 stations throughout the Cook Inlet. At all stations and all depths only methane was observed in the sea water, and it appeared to be in approximate equilibrium with methane in the atmosphere.

During and immediately following the Chevron oil spill in the Gulf of Mexico, [7] water samples were collected at near surface, mid-depth, and near bottom for a large number of stations in and surrounding the spill area. Only in those waters known to have emulsified crude oil were measurable hydrocarbons observed using the gas equilibration technique. The highest total dissolved hydrocarbon concentration was 0.2 ppm. The dissolved constituents were principally low-molecular-weight aromatic hydrocarbons.

Partitioning of Hydrocarbons Between The Atmosphere and Natural Waters

When oil is discharged onto a water surface the lower-molecular-weight hydrocarbons with up to at least 12-15 carbon atoms in the molecule evaporate into the atmosphere rather quickly [8]. Portions of the lower-molecular-weight hydrocarbons also dissolve in water [7]. The amount of dissolved hydrocarbons is generally low.

It has been postulated that up to 90 x 10^6 tons of volatile petroleum hydrocarbons are discharged to the atmosphere each year and an estimated 10% returned to the oceans through rain out [9].

The analytical method described above makes it possible to predict the distribution of hydrocarbons between the atmosphere, fresh water, and sea water [10]. To evaluate what may happen to volatile hydrocarbons discharged onto water and to those hydrocarbons which are released to the atmosphere, equilibrium distributions of representative hydrocarbons in fresh and sea water for various volume ratios of gas to water were calculated and are shown in Table I. The partitioning has been substantiated experimentally for a number of the hydrocarbons [11].

The data in Table I demonstrate that as the gas-water volume ratio increases, the percentage of total hydrocarbon increases in the gas phase. The various classes of hydrocarbons partition according to their solubilities in water relative to their vapor pressures. Thus, partitioning into the gas phase decreases in the order alkanes, olefins, cycloalkanes, and aromatics. Within a given hydrocarbon class type and for a given gas-water volume ratio, hydrocarbons partition more into the gas phase as molecular weights of the hydrocarbons increase.

One-half of the earth's atmosphere exists between its surface and 18,000 feet (5,500 m); the average depth of the ocean is 8,600 feet (2,600 m). Thus, the volume ratio of effective atmosphere to water is approximately 2:1.

The last line of Table I presents the partitioning of the various hydrocarbons between the atmosphere and natural waters assuming equilibrium. Even at equilibrium, almost all of the low-molecular-weight hydrocarbons (up to 12 carbon atoms in a molecule) would be in the atmosphere. The exception is aromatic hydrocarbons, which are approximately equally distributed. However, equilibrium conditions are unlikely because of the long times for their mixing into deeper waters; the effective atmosphere-to-water ratio must be much greater than 2:1. Thus, practically all the lower-molecular-weight hydrocarbons will be found in the atmosphere.

Only a few measurements of low-molecular-weight hydrocarbons have been made in the atmosphere and in ocean waters in remote areas (see [10] for references).

Methane is the single predominant hydrocarbon in the atmosphere and natural waters. There is substantial agreement on the concentration of methane in the atmosphere and worldwide it appears to range between 1.2 and 1.5 ppm. Several investigators have found methane in open ocean or other remote waters to be in approximate equilibrium with that of the atmosphere (the western Atlantic [12], the Atlantic Ocean west of Ireland [13], and the Cook Inlet [6]).

Table I. Partitioning of selected hydrocarbons between different volumes of gas and waters (percentage in gas phase).

	HYDROCARBONS											
	Normal Alkanes				Alkenes			Cycloalkanes		Aromatics		
Gas-Water Ratio	Methane	Ethane	Pentane	Decane	Propene	1-Hexene	1-Octene	Cyclo-pentane	Methyl-Cyclo-Hexane	Benzene	Toluene	Ethyl-Benzene
						Fresh Water						
1:10	72.9	67.0	83.7	98.2	46.2	62.0	78.9	27.4	60.8	2.2	2.6	3.3
1:5	84.3	80.3	91.1	99.1	63.2	76.6	88.2	43.0	75.6	4.3	5.1	6.3
1:1	96.4	95.3	98.1	99.8	89.6	94.2	97.4	79.0	93.9	18.5	21.2	25.3
5:1	99.3	99.0	99.6	100	97.7	98.8	99.5	95.0	98.7	53.2	57.4	62.8
10:1	99.6	99.5	99.8	100	98.9	99.4	99.7	97.4	99.4	69.4	72.9	77.2
						Sea Water						
1:10	79.4	74.3	88.0	98.7	55.1	70.0	84.2	35.0	68.8	3.1	3.7	4.6
1:5	88.4	85.3	93.6	99.4	71.1	82.3	91.4	51.9	81.5	6.1	7.1	8.9
1:1	97.5	96.7	98.7	99.9	92.5	95.9	98.2	84.4	95.7	24.5	27.8	32.7
5:1	99.4	99.3	99.7	100	98.4	99.1	99.6	96.4	99.1	61.8	65.8	70.8
10:1	99.7	99.7	99.9	100	99.2	99.6	99.8	98.2	99.5	76.4	79.4	82.9
2:1	98.7	98.3	99.3	99.9	96.1	97.9	99.1	91.5	97.8	39.3	43.5	49.3

Other low-molecular-weight hydrocarbons have not been found in the atmosphere and open sea water in expected concentrations if a buildup was occurring with time. This suggests that these hydrocarbons discharged to the environment undergo chemical or biological alterations. Photooxidation probably is the principal destructive mechanism for hydrocarbons in the atmosphere, and biodegradation for hydrocarbons in aqueous media.

Extensive measurements with a highly sensitive marine seep detector which measures C_1 through C_4 hydrocarbons in the sub parts per trillion range has failed to show a buildup of these hydrocarbons in sea water [14].

Thus, the evidence suggests no buildup of C_1-C_{12} hydrocarbons in either the atmosphere or natural waters.

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Key Words: Distribution coefficient, Environmental surveys, Equilibration, Gas chromatography, Hydrocarbons in atmosphere, Hydrocarbon types, Hydrocarbons in water, Partitioning of hydrocarbons.

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SUSPENSIONS OF CRUDE OILS IN SEA WATER: RAPID METHODS OF CHARACTERIZING LIGHT HYDROCARBON SOLUTES[1]

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Analytical methods for determining volatile hydrocarbons dissolved in aqueous media using gas chromatography have been summarized by McAuliffe [1]. In addition to direct injection techniques, these include concentration by solvent extraction and gas equilibration. Methods using gas equilibration of water samples have provided analytical sensitivity well under one part-per-billion for individual hydrocarbon compounds [2]. A similar approach by Brooks, et al. [3] permitted determination of methane concentrations in the Gulf of Mexico in the parts-per-trillion range. However, differences in hydrocarbon vapor pressure require repeated gas equilibration for quantitation of the full range of soluble hydrocarbon compounds. Combination gas chromatographic and mass spectrometric methodologies were utilized by Boylan and Tripp [4] to identify components of crude oils and kerosine extracted into sea water. In addition to methods involving gas chromatography, spectroscopic methods for the determination of hydrocarbons in sea water have been reported in the recent literature. Brown, et al. [5] have reported the use of infrared spectroscopy to determine the extractable organic content of deep sea water. Fluorescence spectroscopy has been used by Levy [6] to measure trace quantities of oil in marine waters. These optical methods, however, relate to the analysis of heavy hydrocarbon residues.

The purpose of this study was to develop rapid means for analysis of dissolved light hydrocarbons with respect to hydrocarbon type, which would be suitable for characterization of bioassay treatment media and oil/water discharges of a similar nature. To accomplish this, it was also necessary to develop methods for sampling at locations remote from analytical instrumentation, and for correlation of hydrocarbon composition with simple spectrophotometric methodology. Accordingly, a rapid gas chromatographic method was developed to determine the light hydrocarbon composition of oil/seawater systems. A filtration technique was investigated as a means of removing interfering insoluble hydrocarbons from water prior to analysis. The results of the gas chromatographic analyses were then compared with infrared absorbance data to determine the potential of the IR technique for routine monitoring measurements.

Experimental

Crude oils utilized for these studies were South Louisiana crude, a well-characterized American Petroleum Institute reference oil [7], and Prudhoe Bay crude, which has been studied in some detail by the U. S. Bureau of Mines [8].

Preparation of oil/water mixtures for study followed three general procedures. In the first procedure, a crude oil/seawater mixture (1:45) was shaken vigorously with sea water in a separatory funnel for five min, allowed to stand for 30 min and filtered with pressure through 0.45 μ filter previously solvent extracted to remove interfering organic material. In the second procedure, oil/water mixtures in the same volume ratios as above, were agitated in Teflon-sealed bottles with a mechanical shaker for a minimum of thirty min, the phases allowed to separate at seawater temperature (9°C) overnight, and the aqueous layer drawn off using a glass syphon. The mixtures prepared by the above two procedures were diluted with additional sea water to obtain concentration ranges appropriate for study.

The third type of oil/water mixture was prepared by metering the crude oil into a tank containing flowing sea water while vigorously stirring with an electrically-driven impeller. The bulk of the insoluble oil was allowed to overflow a standpipe, and the mixture of interest, containing soluble hydrocarbon and small oil droplets, was drawn off from below. A range of concentrations of oil in water was prepared by appropriate adjustments of oil and water inflow, and of mixer stirring speed.

Water samples were extracted with 20 ml of carbon tetrachloride and the extracts drawn off into vials fitted with Teflon-lined caps. Repeated analysis of selected samples showed no detectable change in concentration of hydrocarbon components over a period of several months. Infrared spectra from 3200 cm^{-1} to 2750 cm^{-1} were obtained on the extracts in 10 mm quartz cells.

Gas chromatography was performed on aliquots of the solvent extracts. Two ml of solvent extract was pipetted into a small glass-stoppered vial. To this was added 5.0 μl of a solution of indene (5 μl/ml) in carbon tetrachloride as an internal standard. 3.0 μl was injected onto a 17' x 1/8" stainless steel column packed with 4% carbowax 20M TPA on 100-120 mesh chromosorb W. Instrument conditions were: air, 300 ml/min; hydrogen, 30 ml/min; nitrogen carrier, 40 ml/min at a column head pressure of 40 psi. The column was temperature programmed at 5°C/min from an initial temperature of 50°C. Instrument detection sensitivity was 4 x 10^{-11} amps.

Results and Discussion

A gas chromatogram obtained from the extract of a filtered suspension of Prudhoe Bay crude oil in sea water is shown in Figure 1. Under the conditions used, the benzene peak appears high

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[1] This work was supported by Battelle, Pacific Northwest Laboratories through an internal research and development grant.

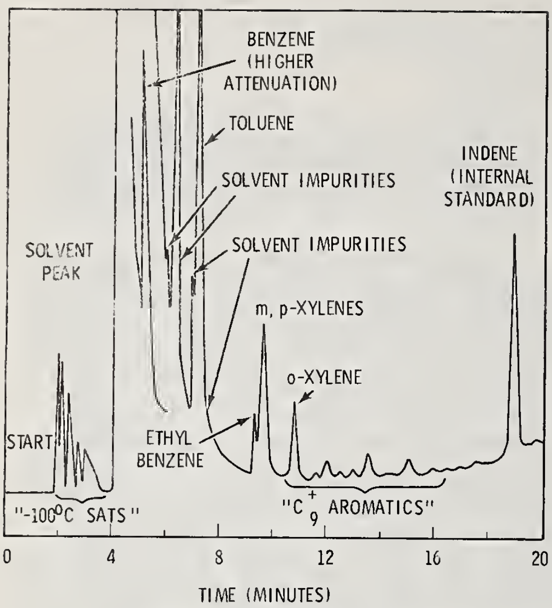

Figure 1. Gas Chromatogram of CCl_4 Extract of Bioassay Water

on the solvent tail and is normally off-scale. However, satisfactory integration of all hydrocarbon components could be accomplished with an Autolab^R computing integrator, permitting an unattended analysis. Compounds emerging after o-xylene were not separately identified and are designated as "C_9+ monoaromatics". Saturated hydrocarbons with boiling points of 100°C or less emerge before the solvent peak. An estimate of these "-100°C sats" was made using the response of n-heptane as a reference.

The appearance of the carbon tetrachloride peak at a retention time intermediate to those of the light saturates and the aromatic compounds permitted a rapid estimation of hydrocarbons by compound type. Total time required for the chromatogram, including instrument recycle, was 35 min. Limits of detection of components in water samples of one-half liter were approximately 0.01 mg/l with the exception of benzene. The position of the benzene peak on the solvent tail precluded detection at levels below about 0.1 mg/l.

The gas chromatographic methodology used for this study was found to be applicable to unfiltered water samples containing on the order of 1 mg/l dissolved hydrocarbons, and not containing appreciable (> 30 mg/l) quantities of insoluble (unfilterable) oil. The presence of more than this amount of insoluble oil in the sample seriously interfered with the analysis by contributing nonaromatic peaks in the aromatic region of the chromatogram, and by interfering with the internal standard peak. Pressure filtration of the water sample through 0.45 μ filters effectively removed these sources of error; however, the use of the filtration technique introduced the possibility of low reported values for soluble hydrocarbons because of mechanical and evaporative losses.

The extent of soluble hydrocarbon losses brought about by pressure filtration was investigated using both infrared and gas chromatographic methods. In the first study, one-half of a filtered aqueous extract of Prudhoe Bay crude oil was filtered again, and the two halves extracted with carbon tetrachloride. Losses of hydrocarbon were estimated by comparing the infrared absorbances. The results of three such experiments indicated that at least 85% of dissolved hydrocarbons could be recovered using the filtration technique. Comparative gas chromatographic analyses of filtered and unfiltered Prudhoe Bay crude-seawater mixtures generated using the "mixer/settler" apparatus are shown in Table I. The component analyses of unfiltered and filtered

Table I. Comparison of Gas, Chromatographic Analyses of Filtered and Unfiltered Samples from "Mixer-Settler" Discharges (CCl_4 Extracts)

	COMPONENT CONCENTRATION (mg/l)					
	24.9 mg/l TOTAL OIL		12.9 mg/l TOTAL OIL		6.6 mg/l TOTAL OIL	
COMPONENT	UNFILTERED	FILTERED	UNFILTERED	FILTERED	UNFILTERED	FILTERED
-100°C SATS	2.90	1.79	0.92	0.61	0.35	0.22
BENZENE	0.20	0.15	-	-	-	-
TOLUENE	0.69	0.63	0.34	0.36	0.14	0.14
ETHYL BENZENE	0.11	0.08	0.04	0.04	0.03	0.01
M, P-XYLENES	0.45	0.40	0.26	0.20	0.11	0.08
O-XYLENE	0.15	0.14	0.09	0.07	0.04	0.03
C_9+ MONOAROMATICS	0.75	0.24	0.40	0.13	0.09	0.03

extracts again demonstrate good recovery of hydrocarbon components with the exception of the C_9+ monoaromatics. The much higher values reported for the C_9+ monoaromatics are a result of interference from insoluble (filterable) nonaromatic components. Losses of saturates upon filtration are somewhat higher than those for aromatic compounds, a reflection of their higher vapor pressure.

Extraction of oil/seawater mixtures with carbon tetrachloride afforded an opportunity to investigate quantitative relationships between hydrocarbon composition as determined by gas chromatography and the corresponding infrared spectra. Figure 2 shows examples of spectra for whole Prudhoe Bay crude oil in carbon tetrachloride, and for extracts of unfiltered and filtered seawater extracts of the crude.

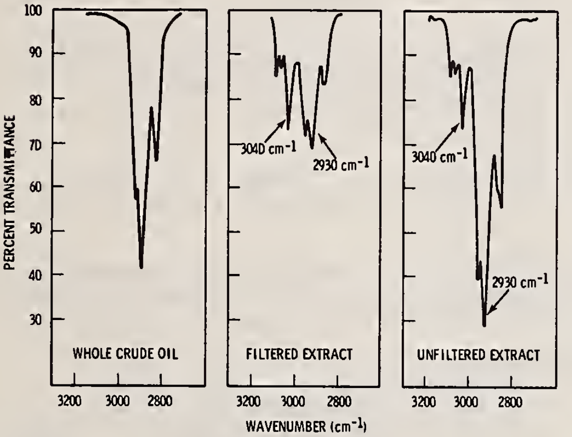

Figure 2. Infrared spectra of Prudhoe Bay crude, and filtered and unfiltered seawater extracts of Prudhoe Bay crude

The spectra obtained from the seawater extracts exhibit sharp bands at 3040, 3070, and 3090 cm^{-1} which do not appear in solutions of the whole crude. These bands characteristic of alkyl substitution on aromatic rings [9] have been used by Frankenfeld [10] to qualitatively estimate losses of light aromatics from crude oils during the process of weathering. The enhancement of absorption in this region occurring in aqueous extracts of oil is a result of the greater solubility of aromatic hydrocarbons than saturate molecules having equivalent mole volumes [11]. The reduction in absorbance at 2930 cm^{-1} of the filtered sample relative to unfiltered is interpreted to be a consequence of evaporation losses, and removal of higher molecular weight saturate hydrocarbons, which are "accomodated" in the sea water [12] rather than in true solution.

Figure 3 shows the relationship established between the concentration of total monocyclic aromatics as determined by gas chromatography, and the absorbance at 3040 cm^{-1} per liter of water extracted. A similar comparison between

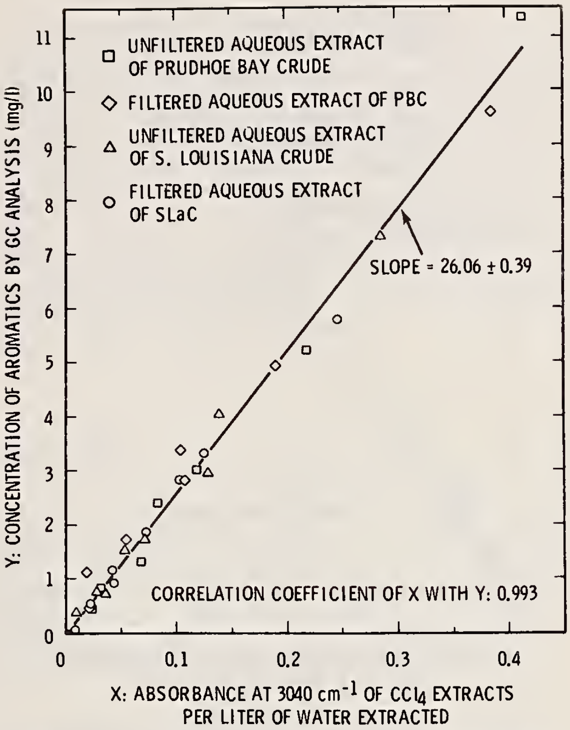

Figure 3. Correlation of aromatics concentration in seawater extracts with infrared absorbance at 3040 cm^{-1}

saturate content and absorbance per liter at 2930 cm^{-1} is shown in Figure 4. The high values of the correlation coefficients obtained is good evidence that quantitative estimates of concentrations of hydrocarbon types can be made by referring to the infrared absorbances of carbon tetrachloride extracts at the appropriate wavelengths.

It is important to note that application of infrared absorbance measurements to compound-type analysis of hydrocarbon solutes is limited to those mixtures containing negligible quantities of insoluble oil, since absorbance from the whole oil masks the contribution to the spectra of the light hydrocarbon components. The filtration technique which was applied to gas chromatographic analysis was, therefore, investigated as a means of removing insoluble oil droplets prior to determination of compound-type distribution by infrared spectrophotometric means. Thus, generated by the "mixer-settler" apparatus, mixtures containing up to 70 mg/l of suspended petroleum, were filtered, and the infrared absorbance of solvent extracts compared with the determined concentrations of hydrocarbon types as in Figures 3 and 4. Again, linear relationships were established between infrared absorbance and concentration of hydrocarbon type, although in the case of the saturates, the determined slope (6.01 ± 0.32) was significantly different from that obtained previously (3.21 ± 0.13).

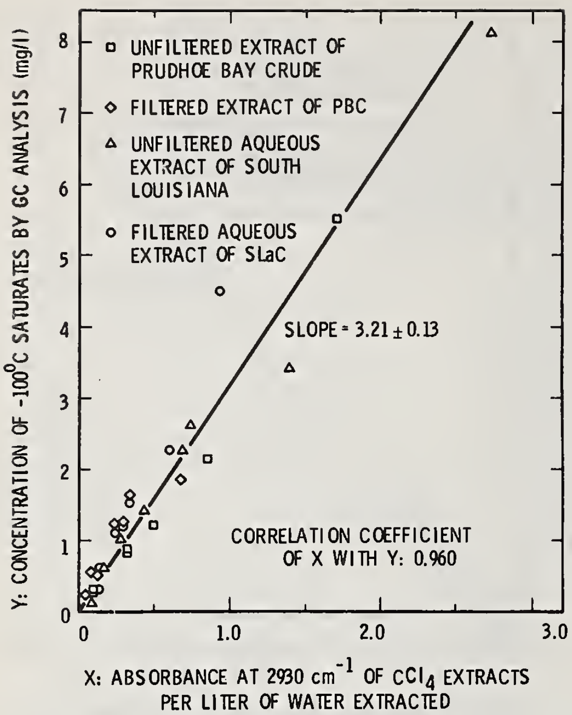

Figure 4. Correlation of saturates ($\leq$ 100°C) in seawater extracts with infrared absorbance at 2930 cm^{-1}

Infrared absorbance measurements on carbon tetrachloride extracts of filtered oil/water mixtures are presently being used to monitor concentrations of light hydrocarbon solutes in toxicity experiments being conducted in these laboratories. As evidenced from the above studies, however, the practical utility of this methodology for routine monitoring is contingent upon first establishing independent data on hydrocarbon composition by other means. The gas chromatographic method developed for these studies appears well suited for this purpose because of the relatively short time required for the analyses.

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Key Words: Crude oil suspensions, Gas chromatography, Filtration of insoluble oil, Hydrocarbon solutions in water, Hydrocarbon type determination by IR, Infrared spectrophotometry.

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MEASUREMENT AND CHARACTERIZATION OF NONVOLATILE HYDROCARBONS IN OCEAN WATER

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A method is described for the measurement and characterization of nonvolatile hydrocarbons (C_{14} and heavier) in ocean water. The method was applied to total dispersed hydrocarbons which generally occur in the concentration range, 0-20 ppb (wt.).

Description of Method

The procedure involves extraction of hydrocarbons from ocean water followed by an infrared measurement of the extracted organics. Following this, the sample is placed on a silica gel column and hydrocarbons are eluted as a fraction(s) which is examined by infrared and ultraviolet absorption spectrophotometers, gas chromatograph and mass spectrometer. Individual steps of the method are shown in Figure 1. In essence, the procedure is based upon extending techniques for handling milligrams to microgram quantities of hydrocarbon. A parallel effort was required to minimize and control contamination so that it could be monitored by judicious use of sample blanks.

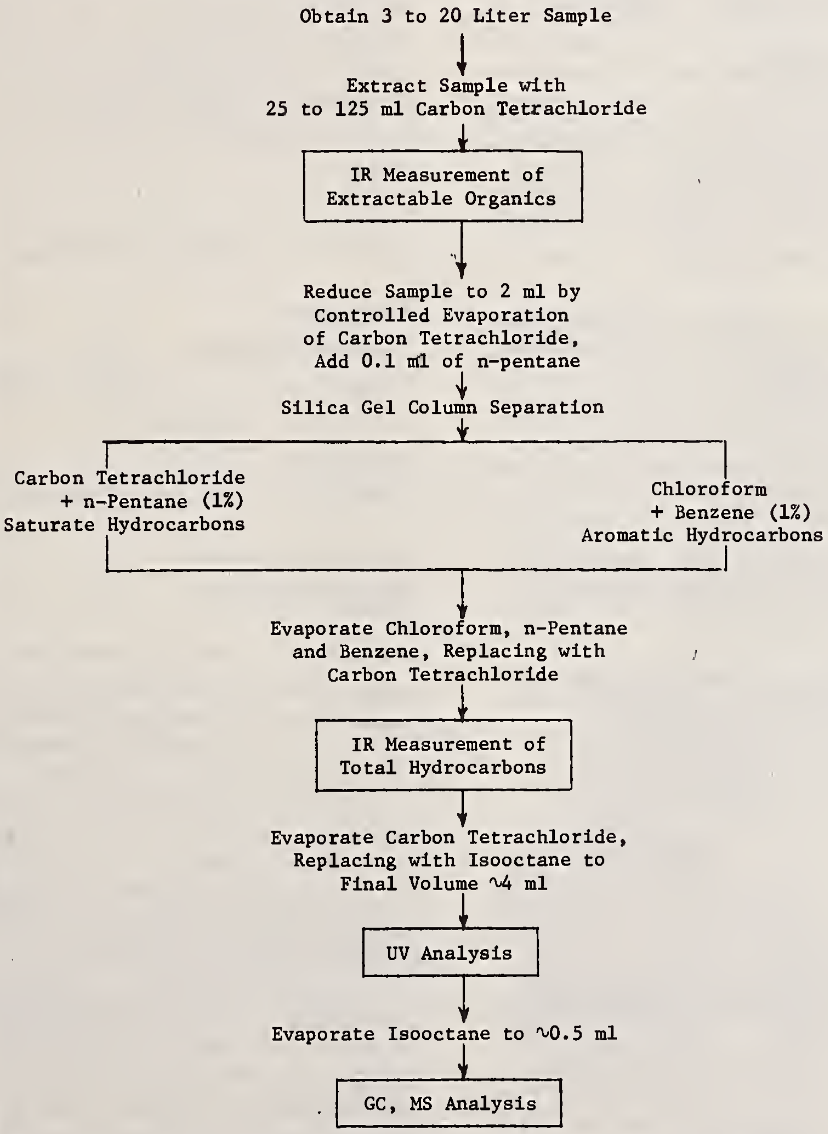

Figure 1. Analytical Method for Nonvolatile Hydrocarbons in Ocean Water.

Practice of the Method

Based on considerable experience, this method is now used to routinely analyze large numbers of ocean water samples. The method is modular in nature and based upon need and/or interest a number of options are available:

- An extractable organic value (hydrocarbons plus other lipids) can be obtained by carrying out the first two steps of the method - extraction and infrared measurement.
- Total hydrocarbons per se or subclassified as saturates and aromatics can be measured by using extraction, silica gel separation and an infrared measurement.
- Hydrocarbon composition can be based on one or all of the techniques - UV spectrophotometry, gas chromatography and mass spectrometry.

Samples to be analyzed are collected from moving tankers or from oceanographic research vessels. From three to nine liter samples of ocean water are extracted with CCl_4 as samples are taken from aboard a tanker. The extract is then sent to the laboratory for final analysis. In order to achieve greater sensitivity, approximately twenty liter samples are usually collected off research vessels. At the time of collection, 25 ml CCl_4 is added to preserve the sample until it can be analyzed.

In measuring and characterizing hydrocarbons, it is the practice to simultaneously handle four unknown samples and a blank. This can be conveniently done by carrying out evaporations on a multi port steam bath and the hydrocarbon separations on a manifold supporting the operation of five silica gel columns. Improved efficiency can also be achieved by queuing up samples for IR, UV, GC and MS measurements. By adhering to this mode of operation, it is possible for a technician to analyze one or more samples a day depending upon the amount of information desired. Extractable organic measurements, for example, may be done at the rate of twelve or more per day.

Considerable work was done to evaluate the efficacy of the method. Information on the key items of interest are listed in Table I.

Table I. Evaluation of Method

Item	Observation
IR Calibration at 2930 cm^{-1}	Average Coefficient = 2.19 ℓ/g cm, variation, 2σ = 28 relative percent. Based on 33 different crude oils.
CCl_4 Extraction	80-111% recovery for known blends of hydrocarbons in ocean water.
Silica Gel Separation	90-100% recovery for known blends of hydrocarbons in CCl_4.
Precision	±10 relative percent for ∿40 μg of hydrocarbons.
Sensitivity	6 μg of hydrocarbon.

Typical Results

The initial steps of the method include CCl_4 extraction of the ocean water followed by an infrared measurement of the organics in the extract. At the level of concentration normally encountered (ppb), these organics include hydrocarbons, esters and acids. Thus, this measurement provides what is defined as an extractable organic value. This parameter is quite useful in base line studies as it represents a maximum hydrocarbon concentration and since it is easily measured it is possible to obtain an overall picture without necessarily determining the hydrocarbon content of every sample.

The magnitude of extractable organic and total hydrocarbon measurements is illustrated by the data in Table II which summarizes results for samples collected along three different tanker routes. These samples were taken from near the top surface of the water using a stainless steel bucket to scoop up the water. Median concentrations of 18-33 ppb and 3-7 ppb were observed for extractable organics and hydrocarbons, respectively. For these median values, hydrocarbons were found to represent from 13-21% of the extractable organics.

Table II. Extractable Organics and Hydrocarbons for Three Tanker Routes

Tanker Route	1	2	3
Extractable Organics			
Range, ppb	10-63	9-67	4-442
Median, ppb	23	33	18
Hydrocarbons			
Range, ppb	2-21	1-22	1-194
Median, ppb	3	7	3.5
Median Hydrocarbons/ Median Extractable Organics	13%	21%	20%

Tanker Route 1 - Gulf of Mexico/New York [1].

Tanker Route 2 - Caribbean/New York [1].

Tanker Route 3 - Intra Mediterranean (La Spezia, Italy/Brega, Libya) [2].

Compositional information is derived from examination of silica gel fraction(s) by UV, GC and mass spectrometer. UV spectra provide insight as to the approximate level of dicyclic and higher aromatic hydrocarbons based on absorption bands at or near 228 nm and 255 nm. Another value of the UV is that zero absorption is a reliable indication for absence of aromatics.

Figure 2 presents some gas chromatograms of hydrocarbons as found in some South Atlantic locations that were sampled for us by the GEOSECS Project. The observed carbon number range of C_{14}-C_{35} is typical. Hydrocarbon type analyses by the mass spectrometer invariably show that saturate hydrocarbons are predominant and consist of paraffins and 1- to 6-ring cycloparaffins. Aromatic hydrocarbons are usually found and consist of

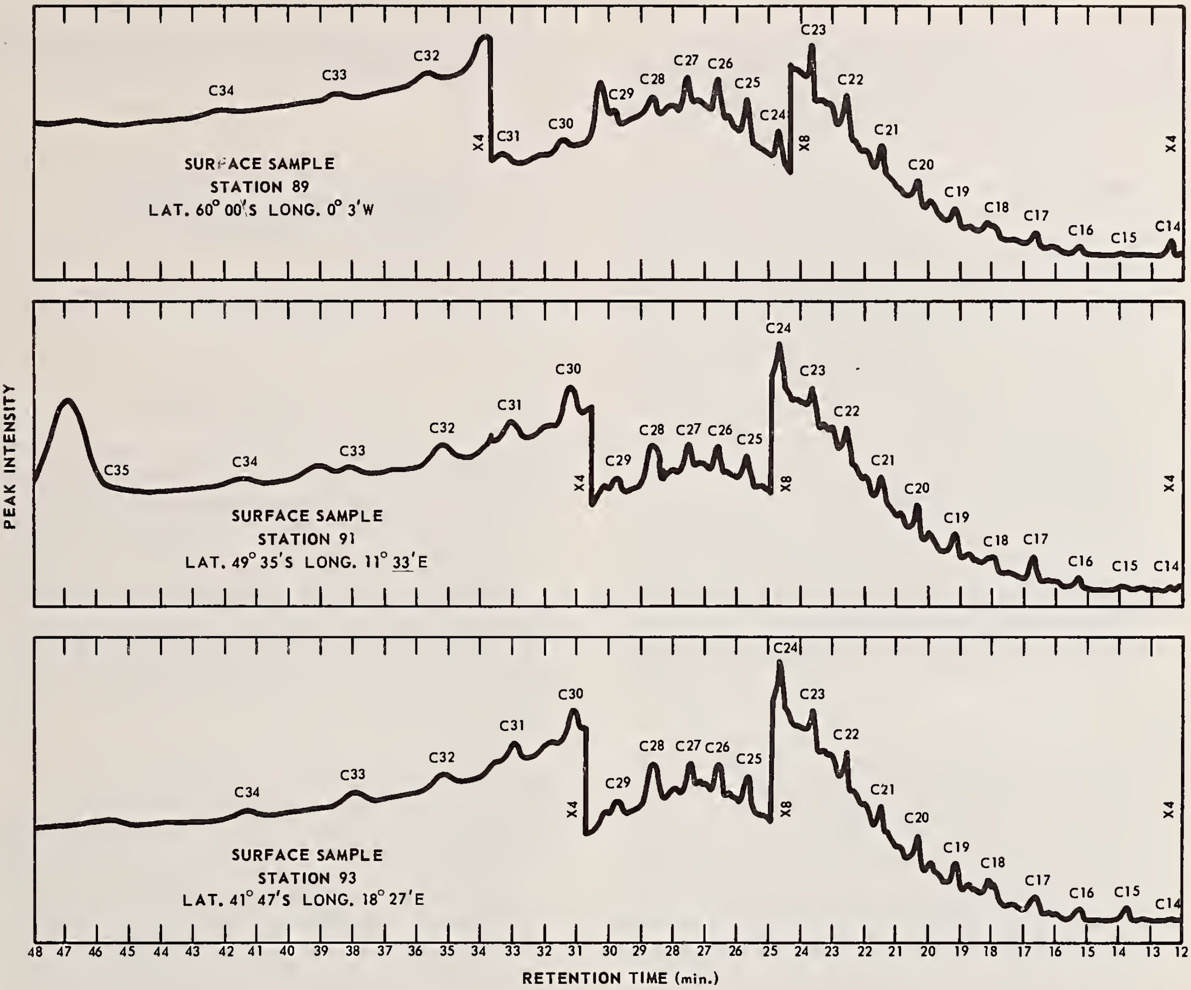

Figure 2. Gas Chromatograms of GEOSECS Samples

1- to 3-ring compounds. Of the samples from the tanker routes listed in Table II that were analyzed for compound types, aromatics were found to comprise from 3-67% of the total hydrocarbons. The median aromatic concentration was 16 percent.

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Key Words: Chromatography, Hydrocarbons Ocean Water; Hydrocarbons Along Tanker Routes; Lipids Along Tanker Routes; Hydrocarbons Ocean Water; Lipids Ocean Water; Measurement Hydrocarbons, Lipids Ocean Water.

NBS Spec. Publ. 409, Marine Pollution Monitoring (Petroleum), Proceedings of a Symposium and Workshop held at NBS, Gaithersburg, Maryland, May 13-17, 1974 (Issued December 1974).

IDENTIFICATION, ESTIMATION AND MONITORING OF PETROLEUM IN MARINE WATERS BY LUMINESCENCE METHODS

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The use of UV-excitation spectrofluorimetry as described by Levy (1) is recommended by IOC/WMO for detecting and measuring dissolved and finely dispersed polynuclear aromatic hydrocarbons in sea water. Levy found that the fluorescence method of analysis is more sensitive and less subject to interference than the simple absorbance method and is therefore superior, especially when the concentrations of residual oils in the sea water are less than 10 ppb. In the remainder of this talk I would like to expand on the potential of luminescence methods, with specific examples.

Luminescence offers a specific and sensitive method for the study of oil in water. The three wavelength parameters of excitation, fluorescence and phosphorescence usually provide sufficient specificity for oil classification. Since the luminescence quantum efficiency of aromatics in oils is usually high, sensitivity is also high. Detection may be remote or in the laboratory on grab samples. The latter allow concentration by extraction and low-temperature analysis. Interferents may be humic materials (Gelbstoffe) or fish oils. The selectivity of the method usually allows discrimination against such interferents.

Identification is best accomplished by studying the Total Luminescence Spectra (TLS) of dilute oil samples. This allows correlation between known and unknown samples, and typing of oils. Low temperature analysis further increases specificity by increased structure and the appearance of phosphorescence. Estimation of oil concentration requires the availability of a known sample, or calibration with another reference method, e.g., infrared analysis.

Surface films, and to some extent dissolved and emulsified oils, may be monitored remotely or via continuous flow systems. All forms of oils, including that adsorbed onto particulates, may be studied by extraction of grab samples into a selected organic solvent.

In the following sections we describe the origin of molecular luminescence and the luminescence characteristics of some petroleum oils. Monitoring methods appropriate to the physical forms of oils present in marine waters are also discussed.

For all practical purposes, molecular luminescence (light emission) occurs only for aromatic molecules, i.e., those having the benzenoid ring system. Examples are benzene, naphthalene, biphenyl, anthracene, and their derivatives.

The physical processes involved in luminescence are shown diagramatically in figure 1. Emission occurs after light of an appropriate wavelength is absorbed by the molecule. The energy absorbed may be re-emitted either as fluorescence or as phosphorescence. Fluorescence is defined as emission which occurs from an excited singlet electronic state (usually the lowest); the lifetime of this emission is very short, usually on the order of nanoseconds. Phosphorescence is defined as emission which occurs from a triplet electronic state (usually the lowest). This emission is of longer wavelength than the fluorescence and is of much longer lifetime; usually the range of 10^{-4} to 10 seconds. Triplet states are significantly populated only by absorption into singlet states, whereupon the molecule undergoes a nonradiative process called intersystem crossing. The longer phosphorescence lifetime makes it more susceptible to quenching so that phosphorescence is ordinarily observed only at low temperatures ($<100^{\circ}$K).

The room temperature fluorescence properties of oils have been studied by many workers (2-9), and the author and co-workers (10, 11) have shown that luminescence analysis at low temperature frequently results in improved sensitivity and selectivity. Crude oils are expected to emit from the near ultraviolet (benzene derivatives) to the deep red (large polynuclear aromatics). Refined oils are expected to emit over a narrower spectral range. Light grades are expected to contain benzene and naphthalene derivatives, which fluoresce in the 300-400 nanometer (nm) region. Heavy fractions contain polynuclear aromatics which would emit at still longer wavelengths. The wavelength of maximum emission will be determined by the relative concentrations, fluorescence quantum yields, and interactions among the emitting components. These expectations are verified in a model oil study undertaken by Baird-Atomic for EPA (12). Figure 2, taken from this study, shows the principal emissions of a naphthenic crude and four oils refined from this crude. These measurements were made front surface on 10u films of undiluted oil using a Baird-Atomic SF-100 Fluorispec spectrofluorimeter. (Spectral intensities obtained with this instrument are not corrected for instrument response.) The lighter oils have their peak emissions near 350 nm, whereas the heavier oils have peak emissions in the 400-500 nm region. The parent crude, which contains all emitting moieties, peaks near 450 nm, intermediate between #4 and #6. The corresponding excitation spectra for these oils (which are related to the absorption spectra) are given in figure 3. These may also be useful for identification or classification.

Spectra of oil films and emulsified oil are expected to be similar if film thickness and particle diameter are similar. Figure 4 shows the principal fluorescence emissions of 11 oils emulsified in deionized water at nominal concentrations of 50 ppm. The mean droplet size for these oils is probably in the 5-10u range. Note in particular that the spectra of #4 oils from two different sources are quite different.

Dissolved oil in marine waters may also be detectable by fluorescence. Marine water samples collected near Gloucester, Massachusetts, were doped with both a #2 fuel oil and a crude. After stirring slowly for a day, samples of the water were removed and transferred to a cuvette for fluorescence analysis. Figures 5 and 6 compare the fluorescence with that of the same oils emulsified in deionized water.

The fuel oil peaks show a small shift to shorter wavelengths in the dissolved sample, but the structure is not greatly changed. This is because the principal fluorescing components in the pure oil are also those which have the highest solubility in water. A much greater change occurs for the crude: The fluorescence of the soluble component is at much shorter wavelengths, and in fact resembles the fluorescence of the #2 fuel. The water-soluble components of the crude are probably chemically similar to those which are responsible for the fluorescence of the fuel. In fact, comparison with the spectrum of naphthalene (fig. 7) suggests that these compounds may be naphthalene derivatives.

Oil present at very low concentrations (sub ppm) in water or biological materials may have to be extracted prior to analysis. Levy (1) and Zitko (13) have described simple fluorescence methods for quantitating oils in marine water and aquatic animals. The use of a solvent generally shifts the principal emission to shorter wavelength because dilution reduces the probability of energy transfer among components.

Although room temperature fluorescence analysis is often useful, even more information can frequently be obtained by observing luminescence at low temperature (typically 77°K, liquid nitrogen temperature). At low temperature (LT), spectral bands generally become sharper and oxygen quenching is reduced, resulting in better sensitivity and selectivity. Figures 8 and 9 show the room and low temperature emission spectra of a crude oil dissolved in methylcyclohexane (MCH) at a concentration of 10 ppm. The spectra show a sharp system originating near 370 nm which is probably due to a pyrene derivative. This fluorescence is largely quenched at RT. The emission peaked near 340 nm at both room and low temperature is probably due to naphthalene derivatives, and LT excitation of the same oil at 380 nm (fig. 10) also shows an emission resembling anthracene.

The phosphorescence emission from oil components may be observed at LT, but not at room temperature under normal circumstances. This emission has a much longer lifetime than fluorescence and can be observed free of fluorescence using a phosphoroscope. Figure 11 shows the luminescence of 10 ppm of an asphalt in MCH at 77°K taken with and without a phosphoroscope. Note that the phosphorescence appears buried in the long wavelength tail of the fluorescence trace.

Oil present as a surface film may also be detected by remote sensing devices. Fantasia and Ingrao (14), Kim and Hickman (15) and Horvath et al (16) describe systems which utilize a nitrogen laser (337 nm) to excite oil fluorescence. A remote sensing device utilizing a low pressure mercury lamp has been reported by Gram (17). A potential disadvantage of monochromatic sources is that certain oils may not be excited efficiently. This difficulty has been overcome in a device described by Eldering and Webb (18) employing a powerful pulsed xenon source coupled to a tunable monochromator, providing variable wavelength excitation. The detection monochromator is also tunable. Emission spectra excited at various wavelengths can be stored, corrected and displayed as contour maps of equal emission intensity. In this format, which we call Total Luminescence Spectra (TLS), changes of oil thickness are readily apparent (figs. 12 and 13).

In the marine environment, several other naturally occurring materials also show fluorescence. These include fish oils, algae (chlorophyll), and Gelbstoffe. The chlorophyll emission occurs near 670 nm, which is at much longer wavelength than the emission maxima of most petroleum oils. Fish oils have fluorescence which occurs in the 350-500 nm region (19), which is in the fluorescence region of many petroleum oils. Gelbstoffe are a complex mixture of water soluble decayed organic material. The intensity and structure of the fluorescence varies somewhat with location, but generally peaks in the 400-450 nm region and typical fluorescence signatures are shown in figure 14 taken from (20).

The sensitivity and specificity (especially at low temperatures) of luminescence analysis of petroleum in sea water suggest practical methods for identifying, estimating and monitoring. Because of the variation of concentrations of luminescence moieties in different oils the simple method of Levy on oil extracts will have to be calibrated for each oil type. A method based on multiple excitation and emission (i.e., the Total Luminescence Spectrum) may be devised to measure a variety of oils. Oils emulsified in sea water may be monitored continuously in a flow system. Active remote sensing instruments, mounted on ships or aircraft, may monitor surface films (and possibly dissolved and suspended oil). Low temperature analysis of TLS of oil extracts provides the most information on identity and concentration. New instrumentation based on the above is currently under development and should be available for test in the near future.

The author wishes to acknowledge the assistance of Dr. J. T. Brownrigg, Dr. D. Eastwood, Dr. B. Dalzell, and Ms. G. Garnick, who performed much of the experimental work and aided in the interpretation of the work reported here. The data were drawn in part from a number of contracts supported by the Environmental Protection Agency, the Coast Guard, the Navy, and NASA.

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Key Words: Analytical methods; Classification of oils; Fluorescence of oils; Identification of oils; Low temperature luminescence; Luminescence of oils; Molecular luminescence; Phosphorescence of oils; Remote sensing; Total luminescence spectroscopy.

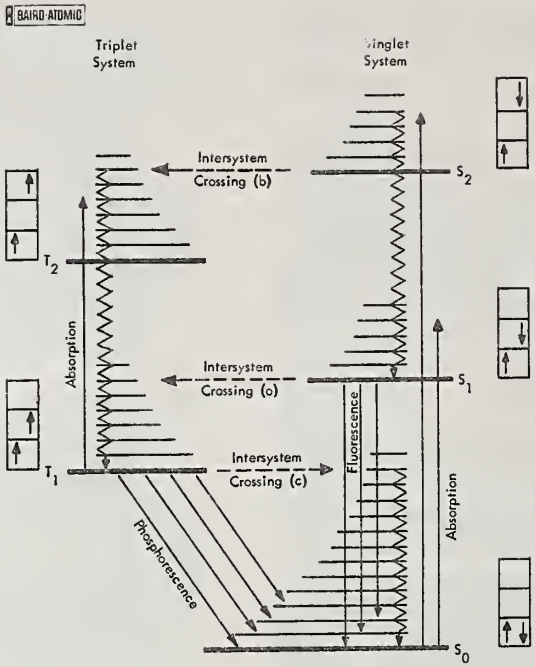

Figure 1. Luminescence Energy Level Diagram.

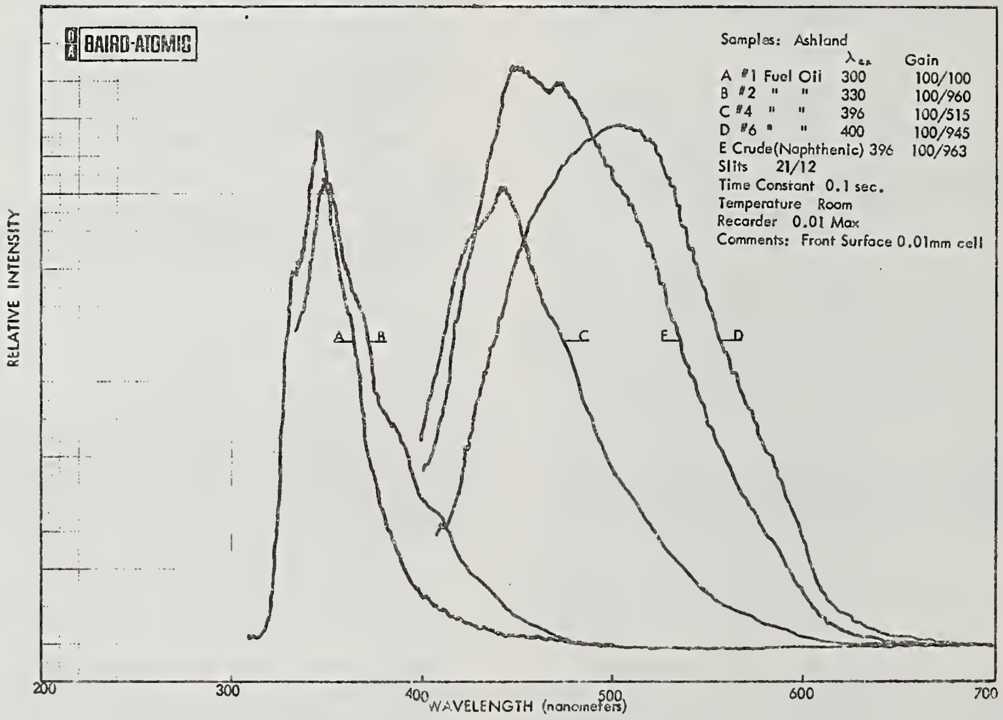

Figure 2. Principal Fluorescence Spectra of Thin Films of 4 Fuel Oils and the Parent Crude.

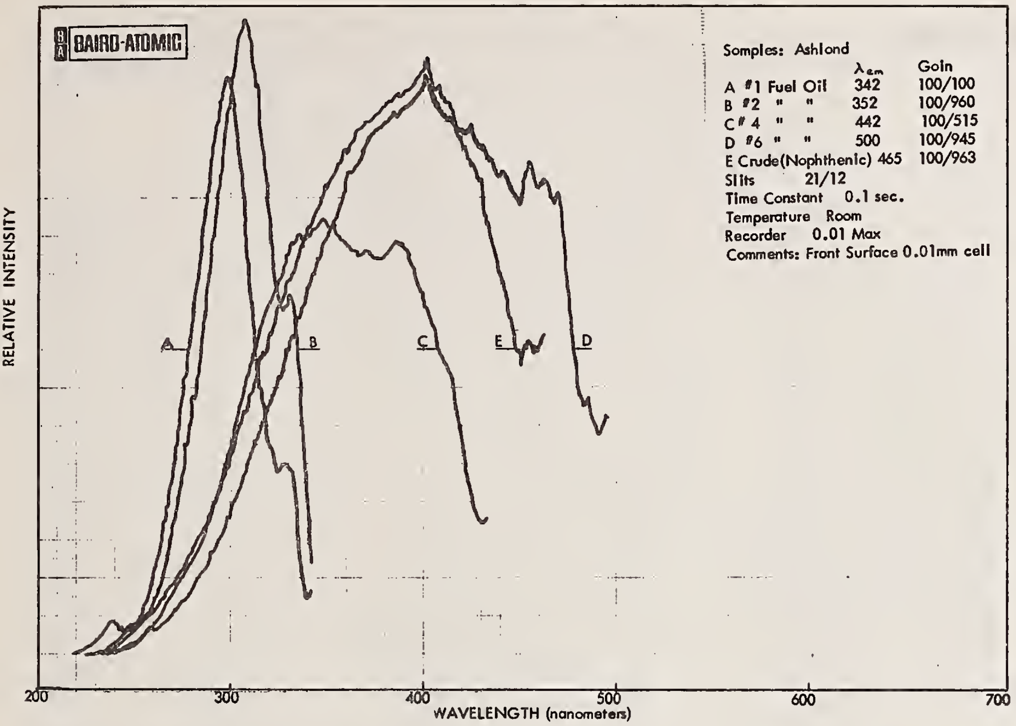

Figure 3. Principal Excitation Spectra of Thin Films of 4 Fuel Oils and the Parent Crude.

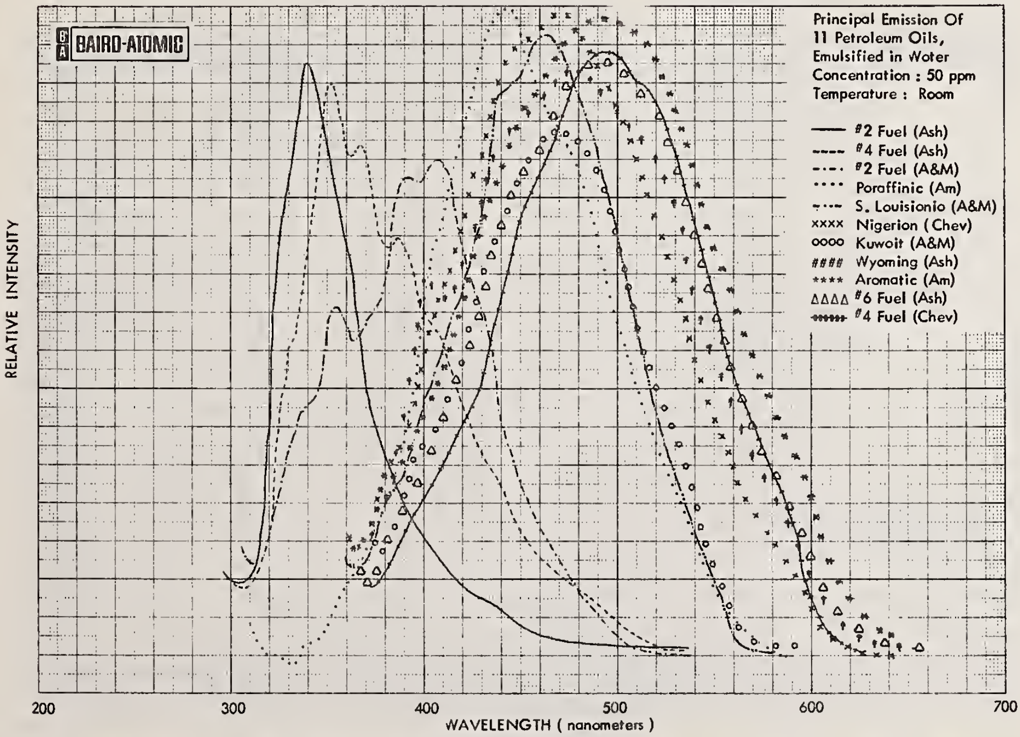

Figure 4. Principal Fluorescence Spectra of 11 Petroleum Oils Emulsified in Water.

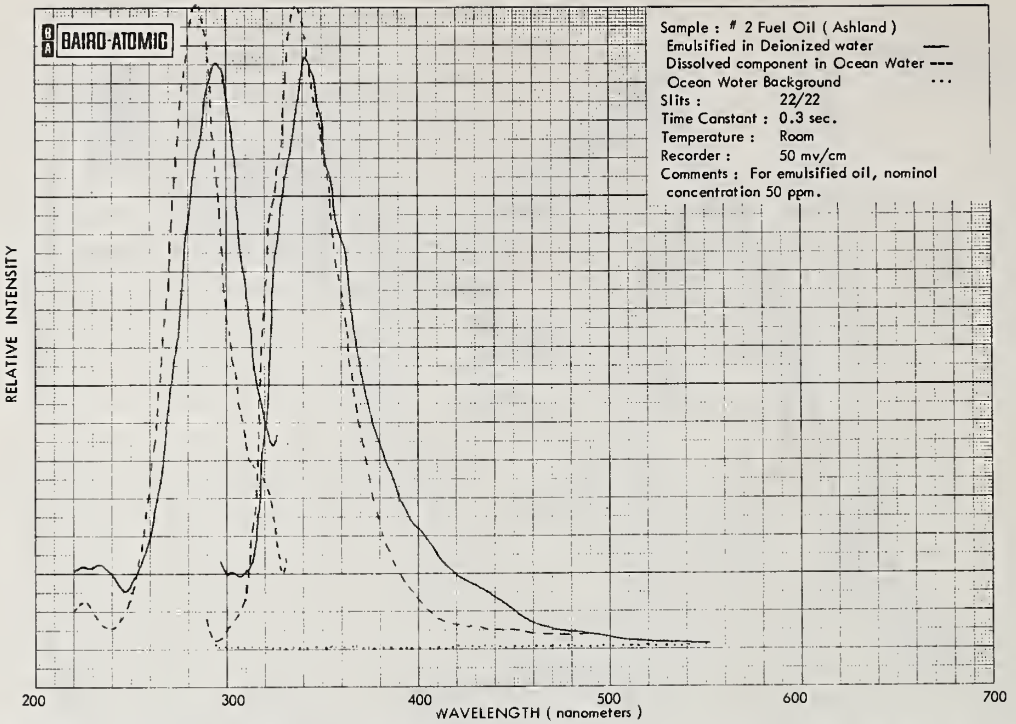

Figure 5. Principal Fluorescence Spectra of a #2 Fuel Oil--Comparison of Water Soluble Fraction with Oil Emulsified in Water.

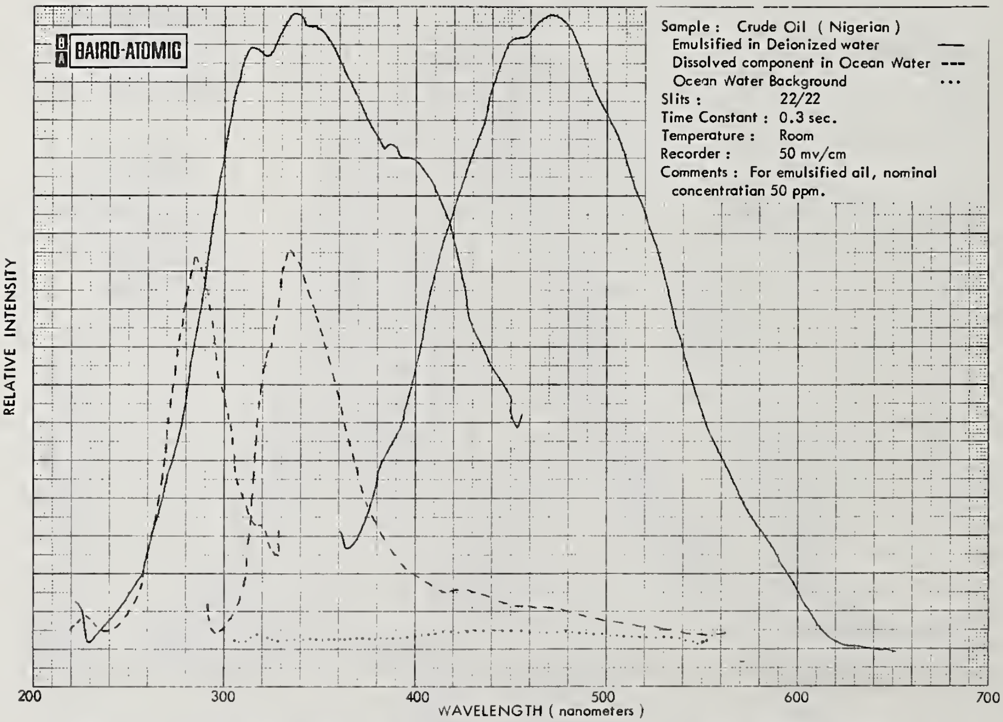

Figure 6. Principal Fluorescence Spectra of a Crude Oil--Comparison of Water Soluble Fraction with Oil Emulsified in Water.

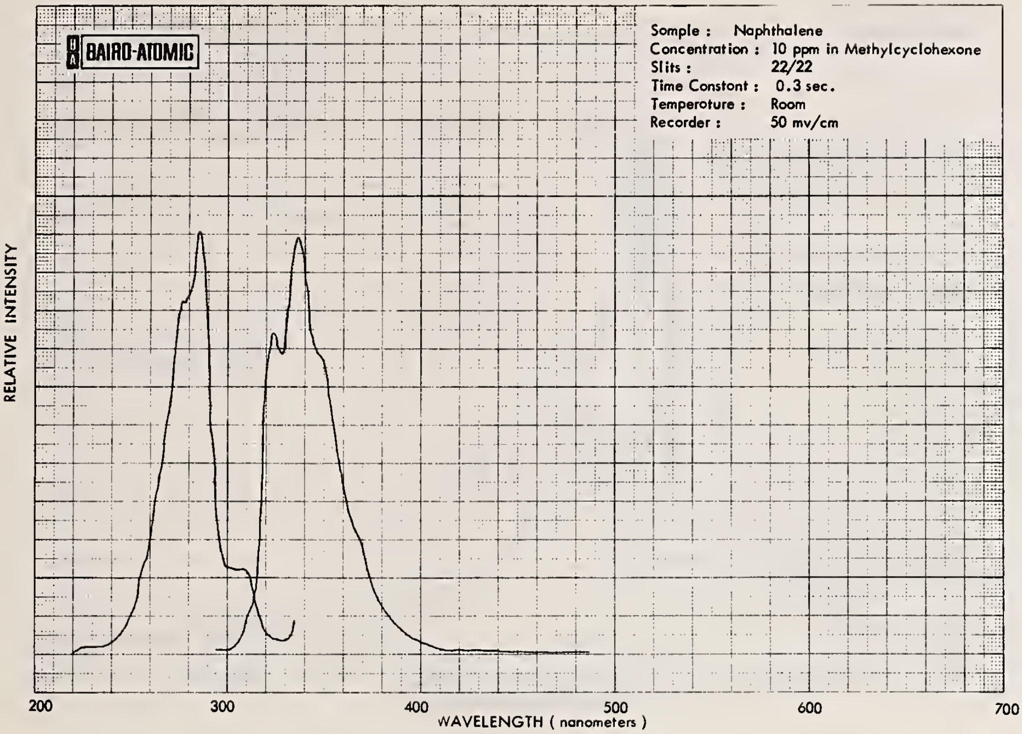

Figure 7. Excitation and Fluorescence Spectra of Naphthalene in Methylcyclohexane, 10 ppm.

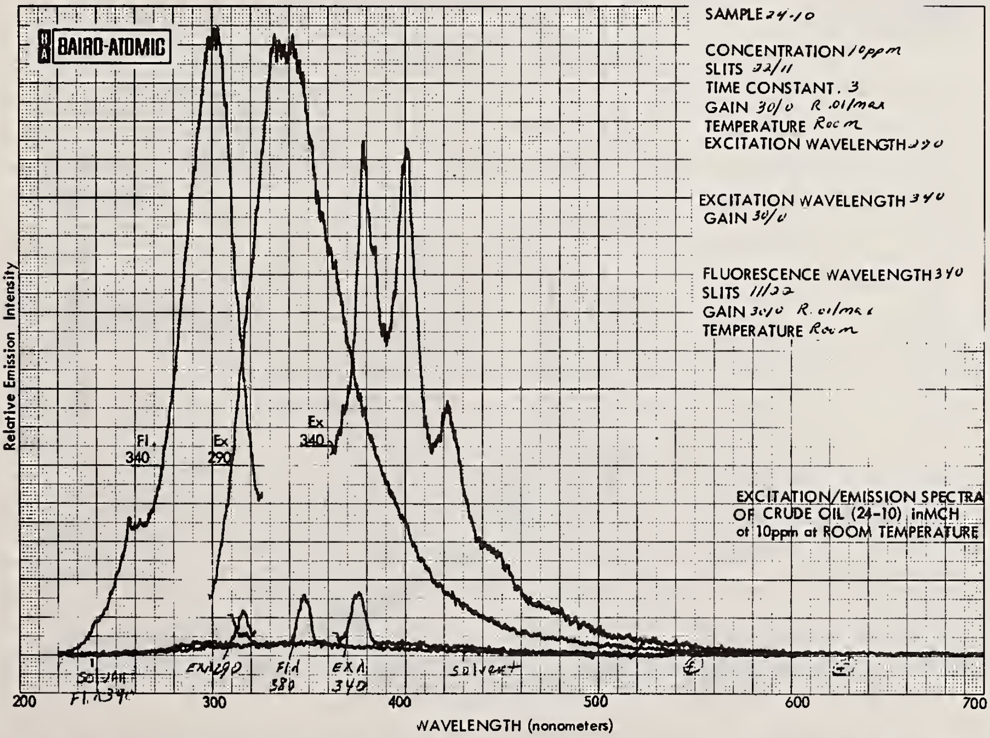

Figure 8. Excitation and Fluorescence Spectra of a Crude Oil (24-10) at Room Temperature.

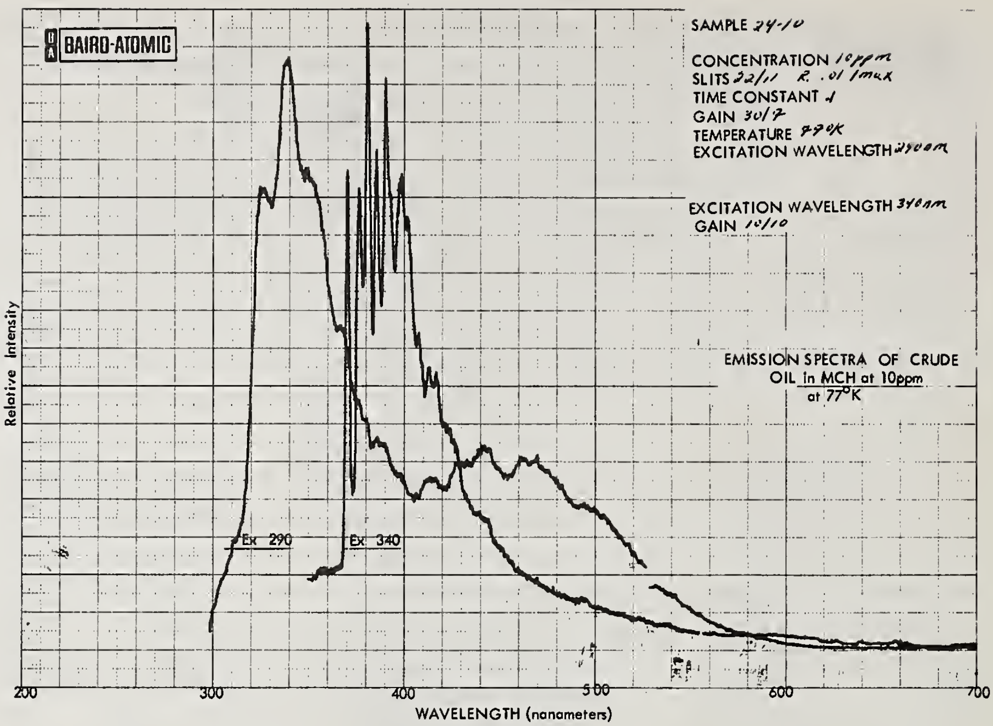

Figure 9. Fluorescence Spectra of a Crude Oil (24-10) at 77°K.

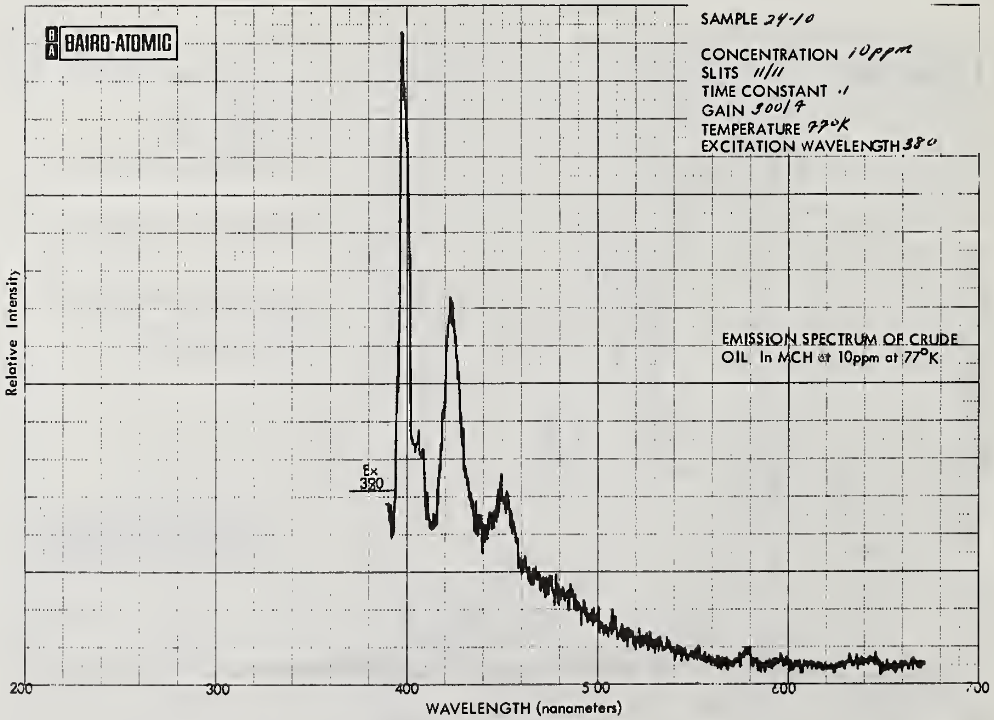

Figure 10. Fluorescence Spectrum of a Crude Oil (24-10) at 77°K Excited at 380 nm.

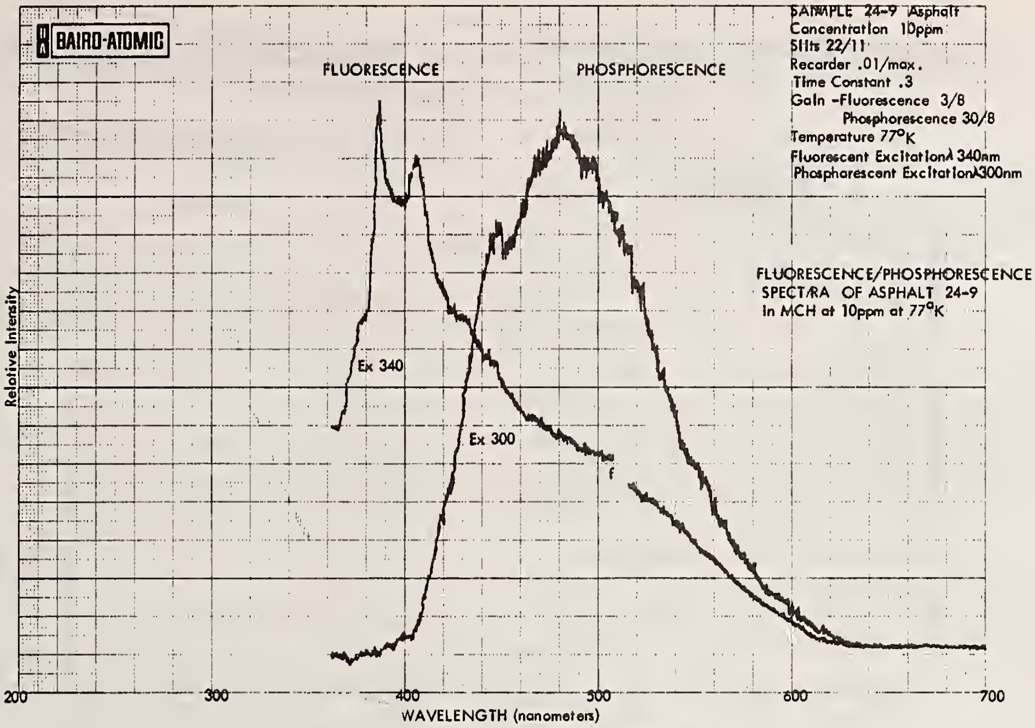

Figure 11. Principal Fluorescence/Phosphorescence Emissions of an Asphalt at 77°K.

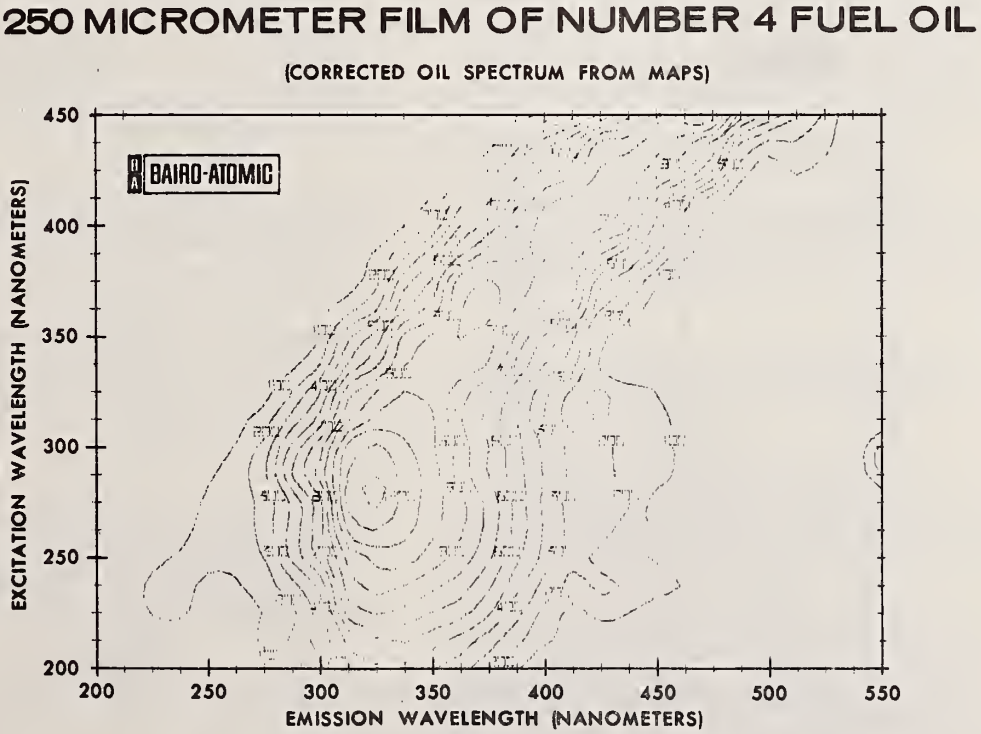

Figure 12. MAPS Luminescence Contour for a #4 Fuel Oil, 250 μm Thick.

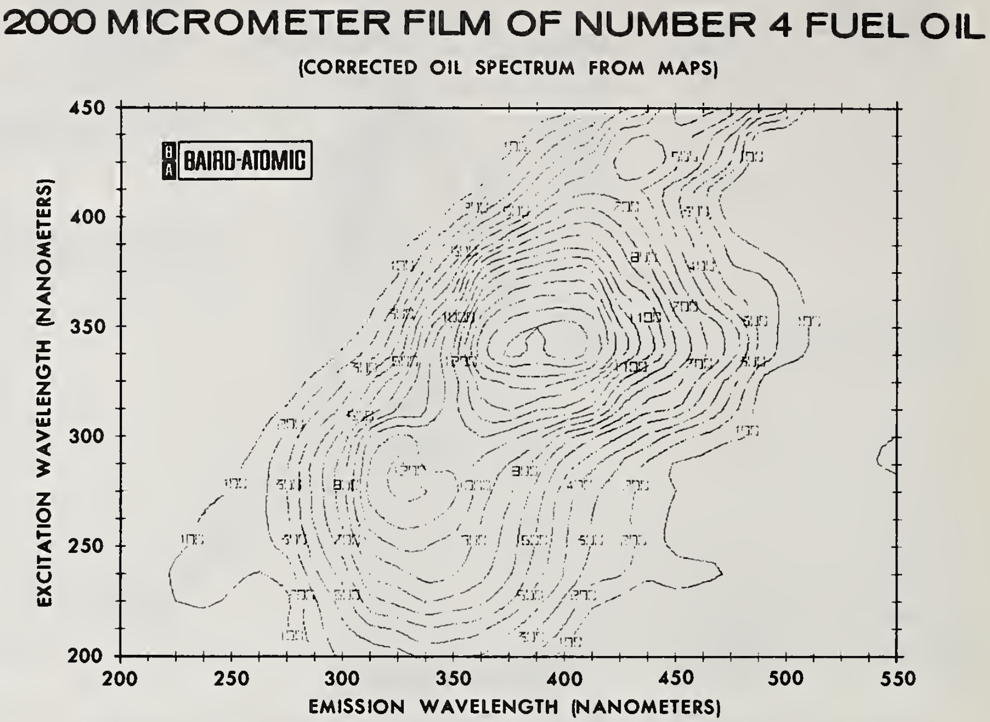

Figure 13. MAPS Luminescence Contour for a #4 Fuel Oil, 2000 µm Thick.

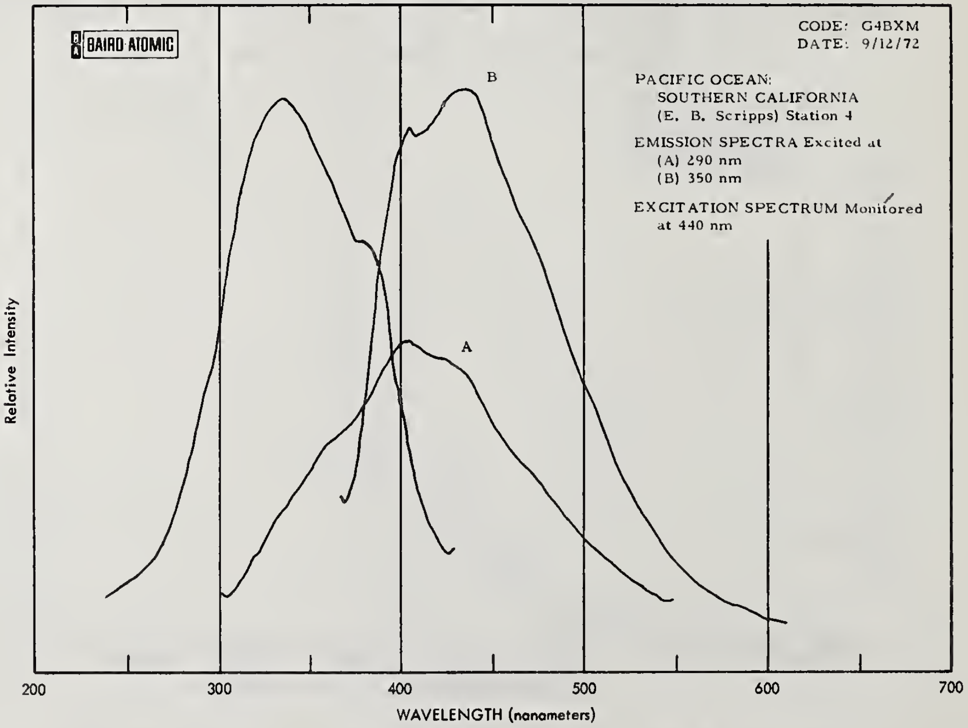

Figure 14. Typical Gelbstoff Fluorescence.

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RECENT DEVELOPMENTS IN THE IDENTIFICATION OF ASPHALTS AND OTHER PETROLEUM PRODUCTS

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INTRODUCTION

The development and testing of a new concept of oil analysis this past year have made possible the first successful application of gas chromatography-electron capture (EC) detector to the analysis and identification of heavy lubricating oils, residual fuel oils and asphalts. Asphaltic materials cannot be readily identified to a source because they are not, by virture of their very high molecular weights and complexity, usually amenable to analysis by gas chromatography with flame ionization detector. The limiting difficulty is the inability to vaporize and to separate the high molecular weight components in the gas chromatographic column. One successful approach leading to their identification is the use of electron capture detector gas chromatography to separate the passively-labeled perfluorobenzyl ether and thioether derivatives of the weak acids present in discharged heavier petroleum products. Use of organic minor components, phenols and mercaptans contained in petroleum, to serve as fingerprints for identification is relatively new and has not been applied toward the identification of petroleum products.

The conversion of weak acids to their respective novel pentafluorobenzyl derivatives and the subsequent EC detector gas chromatographic analysis of certain effluents has provided technical support in enforcement cases, e.g., tracing of phenols found in the city of Wheeling drinking water samples. The procedure, developed at Methods Development and Quality Assurance Research Laboratories, made possible the tracking of minute traces of phenols found in the city water to its source 20 miles upstream.

This paper discloses the successful application of electron capture detector gas chromatography to the analysis of the minor components present in asphalts and their utility to provide prima facie legal evidence, that is corroborated by other methods of identification.

EXPERIMENTAL

PROCEDURE

Collection

The oily, tar-like material was collected by surface skimming of the water surface with aid of a clean wide-mouth bottle. Source samples were obtained from the asphalt pipe line; all samples were preserved in the refrigerator.

Extraction

The water samples (two grams of solid) were extracted with chromatographic grade chloroform (200 ml). Extracts were washed with water, dried over four grams of sodium sulfate and filtered. The filtrate was collected in a 300 ml round bottom distillation flask.

Concentration

The round bottom flask containing the dried chloroform extract was attached to an all glass distillation set-up; using a nitrogen ebullator fitted to a Claisen head. The solvent was evaporated off at 200 mm pressure and collected in a glass receiver leading to a dry ice trap and then to the reduced pressure source.

Completeness of chloroform removal was monitored by disappearance of infrared absorption at 8.22μ and 13.20μ. Extracts of the source material and water samples were treated similarly.

EQUIPMENT

Apparatus

The operating modes of the Perkin-Elmer 137 and 621 infrared spectrophotometers were given previously (2,4). As asphalt petroleum samples are tacky and viscous, thin-films were cast from $CHCl_3$ solution or by warming of the asphalt and the final thickness of the film was adjusted so that the minimum transmittance of the peak at 1450 cm^{-1} lies in the range of 5 to 15%. Traces of chloroform may be monitored by noting the presence or absence of chloroform peaks.

For the electron capture detector gas chromatographic analysis, the Microtek (Tracor) instrument with the Nickel 63 detector was used as described previously (1).

Chemicals

All solvents were purchased from Burdick and Jackson Laboratory, Inc. and reagents were of special purity grade.

DERIVATIVE PREPARATION AND FRACTIONATION

One gram portions of the spill and source asphalt samples were extracted separately after solution in chloroform (150 ml) using 5% alcohol KOH solution three times (150 ml).

The alkaline extract was acidified with 5% HCl in water and then extracted with $CHCl_3$ three times (100 ml). This extract (100 ml) was stirred with 1.0 grams of powdered K_2CO_3 and then refluxed in presence of excess pentafluorobenzyl bromide reagent in acetone (8% solution). After one hour of reflux, the solvents were removed at 60°C/150 mm. The residue was again taken up with 100 ml of $CHCl_3$, shaken with 15 ml of water in order to hydrolyze the esters. The chloroform layer was dried with Na_2SO_4, and filtered. A 100 mg portion of the residue, containing traces of ether and thioether derivatives of phenols and mercaptans from the asphalt source and spill, was fractionated on a 13 cm. silica gel column (6) filled with 34 grams of Davison 60/80 mesh particles, using successive 100 ml volume of hexane, 10% benzene in hexane, 30% benzene in hexane, 50% benzene-hexane, benzene and ether. Six eluate fractions were collected for GC analysis involving use of electron capture detector.

INFRARED ANALYSIS

Both of the dried samples collected from the source and the river sample were analyzed with use of the Perkin-Elmer 137 infrared spectrophotometer. Spectra were characteristically similar throughout the range from 660 cm^{-1} to 4000 cm^{-1}. The spectra of the source and river samples are shown to be similar by visual examination. The two spectra are shown on Figures 1 and 2.

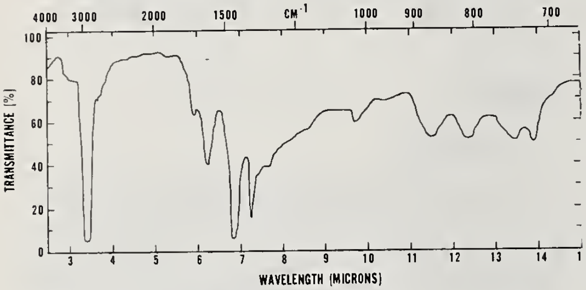

Figure 1. Infrared spectrum of source asphalt.

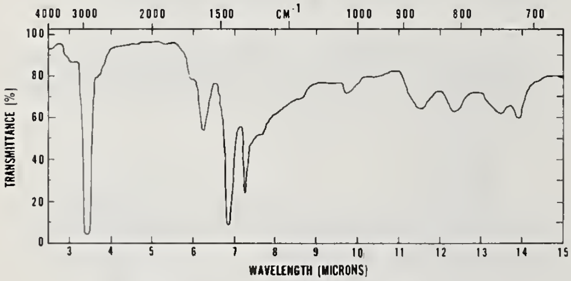

Figure 2. Infrared spectrum of spill asphalt.

Evidence that the source and river samples, are similar is demonstrated by infrared ratios taken of the two samples. These ratios are shown in Table I. A plot of the two key ratios, $\frac{810\ cm^{-1}}{1375\ cm^{-1}}$ vs. $\frac{810\ cm^{-1}}{720\ cm^{-1}}$, obtained on numerous industrial asphalts and No. 6 fuel oils yields the graphical representation shown in Figure 3. The asphalt source ratio and spill ratio lie close-together, indicating identity. They are classified as asphalts as they are located within that group.

Table I. Infrared Ratios of Asphalts
Source - River

Ratio Absorbances	Asphalt Pipeline	Asphalt found in Ohio River
$\frac{720\ cm^{-1}}{1375\ cm^{-1}}$	.32	.32
$\frac{3050\ cm^{-1}}{2925\ cm^{-1}}$	.30	.29
$\frac{810\ cm^{-1}}{1375\ cm^{-1}}$	.28	.29
$\frac{810\ cm^{-1}}{720\ cm^{-1}}$	.86	.89
$\frac{1600\ cm^{-1}}{1375\ cm^{-1}}$	.89	.83
$\frac{1600\ cm^{-1}}{720\ cm^{-1}}$	2.76	2.53

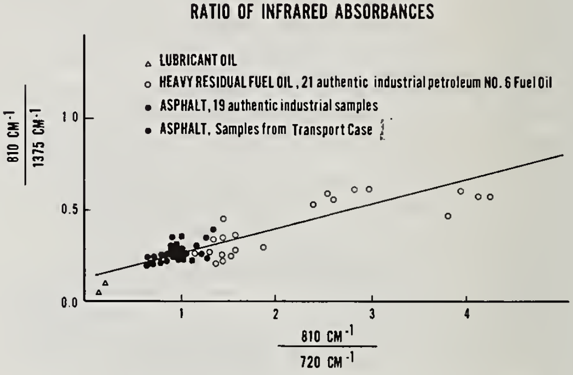

Figure 3. Relationship of the spill and source asphalt among commercial asphalts and No. 6 fuel oils involving two R.I.A.'s.

CARBON-HYDROGEN ANALYSIS

In Table II are shown the carbon and hydrogen determinations of the pipeline asphalt and the Ohio River sample.

Table II. Analysis of Asphalts, Source - River

Parameters	Asphalt from Pipeline	Asphalt from Ohio River
Carbon content %	85.57	86.07
Hydrogen content %	10.86	11.16
Asphaltene[3] %	21.1	22.6
Nickel (μg/g)	81	49
Vanadium (μg/g)	30	28
Za	-5.22735	-4.68050
Zo	-8.40503	-8.92630

he values are averages of seven determinations per sample. This agreement of the carbon and hydrogen content of the pipeline asphalt with the Ohio River sample indicates that the two samples are similar. Determinations were made on the Hewlett-Packard 185B.

GAS CHROMATOGRAPHIC ANALYSIS

The following demonstration is proof that the Ohio River sample is identical to the source sample taken from the asphalt pipeline. To demonstrate that the two are similar, the weak acid components (phenols and mercaptans) of the asphalts taken from the source and from the river were compared. Each asphalt mixture is treated with pentafluorobenzyl bromide and potassium carbonate in an acetone-chloroform mixture. Each reaction mixture is then fractionated into six fractions using solvent mixtures of varying polarity to effect a separation on silica gel column. The third eluate fraction yielded the revealing electron capture detector gas chromatograms, Figures 4 and 5.

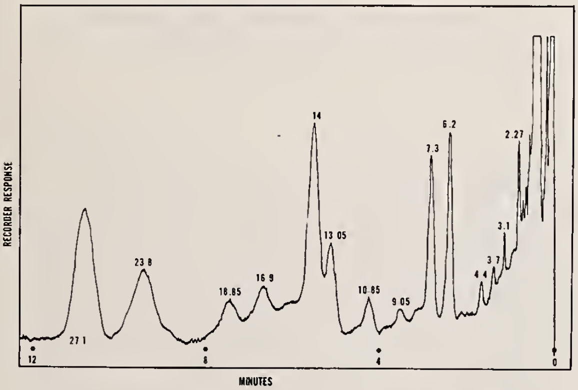

Figure 4. Electron capture gas chromatogram of derivatives of weak acids from source asphalt.

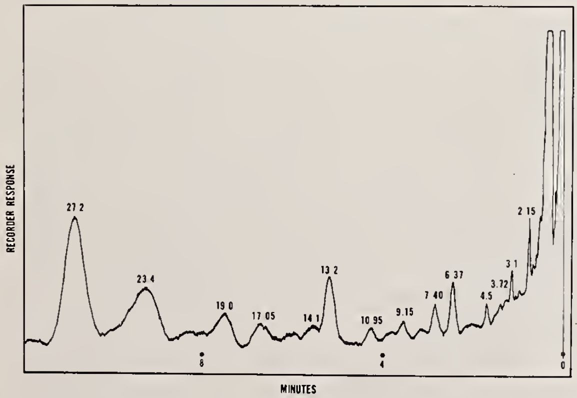

Figure 5. Electron capture gas chromatogram of derivatives of weak acids from spill asphalt.

The retention distance of the 14 resolved peaks taken from the electron capture gas chromatographic analysis of the pentafluorobenzyl derivatives of the asphalt pollutant from the Ohio River were compared to those from resolved peaks of the derivative asphaltic material that was taken from the asphalt pipeline. Fourteen peaks (phenols and mercaptans) of the source sample match the fourteen peaks (phenols and mercaptans) of the pollutant Ohio River sample. All 28 retention distances were plotted as a 45° diagonal line showing excellent agreement of retention distances of the two samples. (Three components of the 14 found in the source samples are larger in amount than in the river sample; these may be lost as a result of solubilization, etc.). The two asphalts are the same.

NICKEL AND VANADIUM RESULTS

The residue of asphalt resulting from the digestion in concentrated nitric acid was dissolved in dilute nitric acid and analyzed by atomic absorption. The nickel and vanadium contents in the source sample were 81 and 30 mg per gram, and these values in the river sample were 49 and 28 mg per gram, respectively. The nickel in the river sample appears to be somewhat lower than expected, whereas the vanadium results agree well (Table II).

DATA TREATMENT AND STATISTICAL ANALYSIS

Infrared spectrophotometry has been a useful technique for the characterization and identification of these materials. With the use of a combination of infrared spectrophotometry, data treatment, data transformation, and discriminant function analysis with computer assistance, a precise method of classification has been derived (5). From among 20-plus samples of commercial asphalts, the unknown river sample was coupled to the commercial source via good agreement of mathematical values from the corresponding linear discriminant functions (5) as indicated by the Za's values in Table II. Za and Zo are the linear discriminant function values of asphalt and heavy residual fuel oil, respectively. The higher algebraic values belong to Za's. Therefore, both are asphalts. In addition, the fairly close agreement of the Za's values of the source and spill asphalt indicates reasonable identification.

ENFORCEMENT ACTION

The Coast Guard won its case. All results pointed to the conclusion that the pipeline asphalt was the source of the pollutant river asphalt.

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Key Words: Asphalts; Characterization; Computers; Discriminant Function Analysis; Gas Chromatography; Heavy Oils; Identifications; Infrared Analysis; Minor Component Analysis; Oil Spills.

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IDENTIFICATION OF HYDROCARBONS IN AN EXTRACT FROM ESTUARINE WATER ACCOMMODATED NO. 2 FUEL OIL

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Introduction

The traditional use of the oceans, estuaries and other large bodies of water, mainly as a source of food, is increasingly being challenged by other large scale technological operations typical of modern civilization. At the same time, there is a growing need to develop the maximum potential of the oceans as a source of protein. In the shaping battle between the different interests, it is of utmost importance that the scientific community has the sound, basic knowledge necessary to understand the possible interferences of such technological uses with marine food production.

Of concern here are the fossil hydrocarbons and activities capable of affecting their composition and distribution in the environment. Considering the extreme complexity of such mixtures and the resulting complex interactions with the biota, it is clear that a sufficient scientific knowledge base can only be reached within reasonable time by the proper combination of maximum efficiency and analytical limitation. Since analytical limitation is inherent even with the most sophisticated methods of analysis, only those capable of providing a maximum of information and those which lend themselves to computerized data acquisition and interpretation should be used: the mass spectrometer with interfaced gas chromatograph and data handling system. The application of such a system to a problem of hydrocarbon analysis is described.

Analysis of an extract of a No. 2 fuel oil accommodated to water.

A commercial grade No. 2 fuel oil (Gulf) was accommodated to filtered and pre-extracted York River water at room temperature, extracted with methylene chloride [1] in one experiment and with n-heptane [2] in another. These extracts were then submitted to analysis in a computerized GC-MS system with repetitive scan (Finnigan, 1015). Aliquots of the extracts were also used to derive chromatograms using Apiezon L as the stationary phase. To demonstrate the compositional changes occurring in the water accommodation step [3], chromatograms were also derived from straight No. 2 fuel oil, from a 5A molecular sieve accommodated fraction of No. 2 fuel oil and from the residual fraction of the molecular sieve treated fuel oil.

Figure 1a shows the general features of the No. 2 fuel oil; a broad, unresolved envelope with a boiling range extending from about 170°C to 360°C. Superimposed on this envelope are distinct peaks, mainly the n-alkanes (fig. 1b), the isoprenoid pristane (peak No. 40, fig. 1a), plus a number of aromatic compounds, mainly substituted benzenes, 1, 2, 3, 4-tetrahydronaphthalenes and naphthalenes.

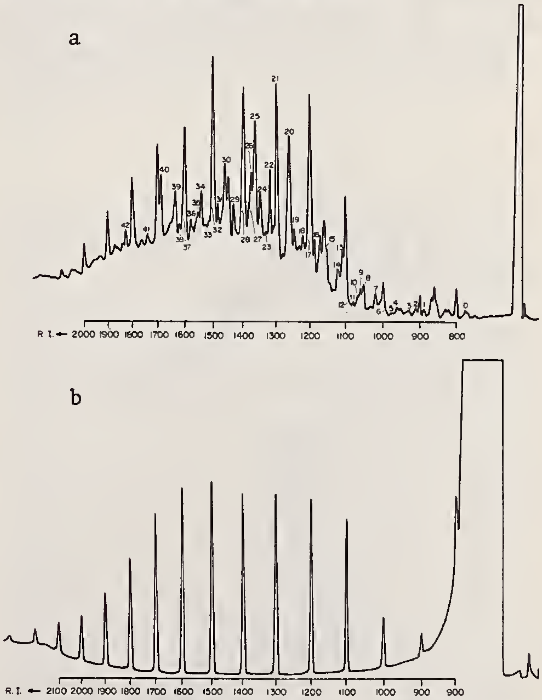

Figure 1a. Commercial No. 2 fuel oil. Numbers refer to corresponding peaks. Abszissa identifies retention indices. 1b. N-alkanes separated from the same fuel oil. Column data: 3% Apiezon L, 80-100 chrom.-W-AW, ss 8 1/2' x 1/16", 5.6 cc/min N_2

In figure 2, the fractionating effect of the water on the oil is clearly demonstrated. Chromatogram 2a is again from No. 2 fuel oil and 2b is from the extract of the water accommodated phase. The unresolved envelope in the extract is almost absent, the main n-alkane peaks have disappeared or are hidden in the large peaks now practically all consisting of aromatic compounds. Identifications in these low resolution chromatograms must be viewed with caution, as many of the peaks contain several compounds. Where reference to compound types or specific compounds is made, it is supported by information from Scot columns and mass spectrometric information. The most prominent peaks are the substituted tetralins (20, 22,24), tetralin (17), biphenyl (29), the substituted naphthalenes (30,31,32), methyl indane (16) and substituted benzenes (0, 1, 2, 6, 7, 8, 13 and 15). Although precise solubilities for most of these compounds are not available, estimates based on empirical relationships [4] suggest that the concentrations of the substituted benzenes in the water tend to follow the solubilities.

The "aromatization" of No. 2 fuel oil upon uptake by water is again seen in figure 3. The top chromatogram (fig. 3a) is the water extract, the bottom chromatogram (fig. 3b) is derived from No. 2 fuel oil by subtraction of all compounds accommodated by 5A molecular sieve. The two chromatograms differ mainly in the large unresolved envelope. Most of the peaks, except for differences in intensity, are identical in both chromatograms. It should be mentioned that all chromatograms from samples involving a solvent evaporation step are distorted (co-evaporation of volatile compounds) and that the actual concentrations of substituted benzenes and indanes in the original samples are considerably higher. In a typical oil spill situation, however, such losses may also occur because of the competition between the relatively fast evaporation and the diffusion limited solubilization at the interface.

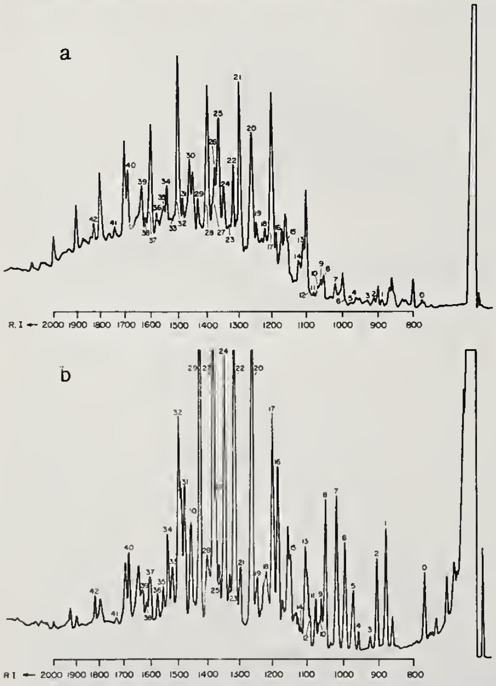

Figure 2a. Same as 1a.
2b. Methylene chloride extract of York River water accommodated No. 2 fuel oil. Column data are the same as in fig. 1.

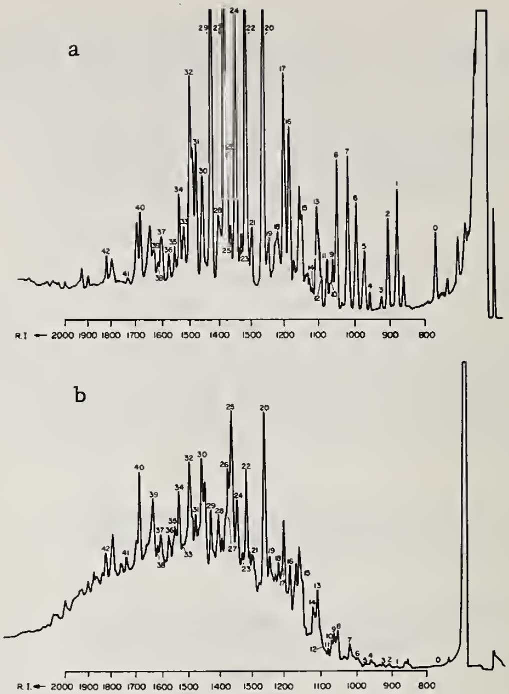

Figure 3a. Same as 2b.
3b. No. 2 fuel oil minus n-alkanes (and other compounds which are accommodated by 5A molecular sieve). Column data as in fig. 1.

The detailed characterization of the water extracts led to the identifications shown in Tables I-III. Two different liquid phases were necessary to produce the displayed detail. Most of the monoaromatics were identified from runs using a DDP coated Scot column (100' x 0.02", 1.5 cc/min helium flow) and the condensed aromatics from a Scot column with OV-25 as the stationary phase (50' x 0.02", 1.5 cc/min helium flow).

Table I shows the alkylbenzenes identified in the water extract. The most reliable identifications are those based on standard samples and are listed under a. Those labeled b have been identified from spectra in the Aldermaston collection

TABLE I.

BENZENE COMPOUNDS FOUND IN A METHYLENE CHLORIDE EXTRACT OF AN ESTUARINE WATER ACCOMMODATE OF A NO. 2 FUEL OIL BY GC - MS

MONOSUBSTITUTED BENZENES, C_7 to C_{10}

a	ETHYLBENZENE	T
	n-PROPYLBENZENE	T
	ISOPROPYLBENZENE	T
	SEC-BUTYLBENZENE	T
	ISOBUTYLBENZENE	T

BISUBSTITUTED BENZENES, C_8 to C_{10}

a	o - XYLENE	
	m - XYLENE	
	p - XYLENE	
	o - DIETHYLBENZENE	
	m -DIETHYLBENZENE	T
	p - DIETHYLBENZENE	
	o - ETHYLTOLUENE	
	m -ETHYLTOLUENE	
	p - ETHYLTOLUENE	
b	o-n- PROPYLTOLUENE	
	p -n-PROPYLTOLUENE	
	o - ISOPROPYLTOLUENE	T
	m - ISOPROPYLTOLUENE	
	p - ISOPROPYLTOLUENE	T

TRISUBSTITUTED BENZENES, C_9 & C_{10}

a	1,2,3 - TRIMETHYLBENZENE
	1,2,4 - TRIMETHYLBENZENE
	1,3,5 - TRIMETHYLBENZENE
b	1,2 - DIMETHYL-3-ETHYLBENZENE
	1,2 - DIMETHYL-4-ETHYLBENZENE
	1,3 - DIMETHYL-2-ETHYLBENZENE
	1,3 - DIMETHYL-4-ETHYLBENZENE
	1,4 - DIMETHYL-2-ETHYLBENZENE

TETRASUBSTITUTED BENZENES, C_{10}

a	1,2,4,5 - TETRAMETHYLBENZENE
b	1,2,3,4 - TETRAMETHYLBENZENE
	1,2,3,5 - TETRAMETHYLBENZENE

C_{11} & C_{12} ISOMERS SEPARATED, NOT SPECIFICALLY IDENTIFIED

			NO.
c	C_5 - SUBSTITUTED BENZENES		16
	C_6 - SUBSTITUTED BENZENE	T	1

T = TRACE, M = MAJOR CONSTITUENT

a INDICATES IDENTIFICATION BY COMPARISON WITH STANDARDS RUN ON SAME GC - MS

b IDENTIFIED BY B.P. & GC RETENTION TIME DATA AND COMPARISON WITH M.S. DATA IN LITERATURE

c CORRELATED WITH M.S. LITERATURE DATA

and have been structually labeled according to their boiling points. Listings under c, finally, are identifications based on mass spectra alone. Admittedly, some of the identifications labeled b and c may not be definitive, as in some cases the mass spectra alone may not be specific enough to identify the compound, or assumed retention trends may prove to be invalid. Where compounds have been separated and partially identified, we did not have adequate information to specify the substituent groups in detail. It is certain that some of these ambiguities will be corrected as work progresses.

In Table I, it is noted that all isomers of diethyl-, methyl- ethyl-, methyl-isopropyl-, trimethyl- and tetramethylbenzene were found. All dimethylethylbenzenes except the 1, 3-5 isomer were identified. Altogether 30 substituted benzenes were identified and 17 more isomers were separated and partially identified but could not be further characterized.

Table II shows the naphthalenes and 1, 2, 3, 4-tetrahydronaphthalenes, again with the mode of identification. The monoalkylnaphthalenes containing either a methyl or ethyl group are complete. Four of the 10 possible isomers of dimethylnaphthalene are not identified with respect to their structure, but 2 more were separated. The missing two isomers were either not present above the detection level or were co-eluting with a relatively abundant compound. Only two of the 15 possible trimethylnaphthalenes could be specifically identified; more may be among the 7 separated C_3 - isomers. All naphthalenes of either higher substitution or molecular weight remain of unknown specific structure because their mass spectra do not allow further distinction. All of the possible methyltetralins were identified and together with the tetralin they belong to the most prominent compounds found in the water extracts. Ethyl-, dimethyl- and trimethyltetralins were separated and identified by their mass spectra, but no specific structure could be assigned. Thus, 18 naphthalenes and tetralins could be characterized completely, while 30 more were separated and partially identified.

TABLE II.

NAPHTHALENE COMPOUNDS FOUND IN A METHYLENECHLORIDE OR HEPTANE EXTRACT OF AN ESTUARINE WATER ACCOMMODATE OF A NO. 2 FUEL OIL BY GC-MS

a	NAPHTHALENE, $C_{10}H_8$	

MONOSUBSTITUTED NAPHTHALENES, C_{11} & C_{12}

a	1- METHYLNAPHTHALENE	M
	2- METHYLNAPHTHALENE	
	1- ETHYLNAPHTHALENE	
	2- ETHYLNAPHTHALENE	

BISUBSTITUTED NAPHTHALENES, C_{12}

a	1,6,& 1,3 - DIMETHYLNAPHTHALENE	M
	1,5 - DIMETHYLNAPHTHALENE	
	2,6 - DIMETHYLNAPHTHALENE	
	2,3 - DIMETHYLNAPHTHALENE	
	1,4 - DIMETHYLNAPHTHALENE	

TRISUBSTITUTED NAPHTHALENES, C_{13}

a	2,3,5 - TRIMETHYLNAPHTHALENE	
	2,3,6 - TRIMETHYLNAPHTHALENE	

C_{12} to C_{15} ISOMERS SEPARATED, NOT SPECIFICALLY IDENTIFIED

		NO.
c	DIMETHYLNAPHTHALENES	2
	C_3-SUBST'D. NAPHTHALENES	7
	C_4-SUBST'D. NAPHTHALENES	8
	C_5-SUBST'D. NAPHTHALENE	1

1,2,3,4-TETRAHYDRONAPHTHALENES (TETRALINS)

b	1,2,3,4-TETRAHYDRONAPHTHALENE, $C_{10}H_{12}$	M

MONOSUBSTITUTED TETRALINS, C_{11}

b	1 - METHYLTETRALIN	
	2 - METHYLTETRALIN	M
	5 - METHYLTETRALIN	M
	6 - METHYLTETRALIN	M

C_{12} & C_{13} ISOMERS SEPARATED, NOT SPECIFICALLY IDENTIFIED

		NO.
c	ETHYLTETRALIN	1
	DIMETHYLTETRALINS	9
	TRIMETHYLTETRALIN	1
	C_3-SUBST'D TETRALIN	1

Table III contains the indanes, biphenyls and a few polyaromatic compounds plus some of their alkylated forms. Most of the latter must remain unidentified with respect to their detailed structure for reasons mentioned above. Also present are the n-alkanes from decane to tridecane, and finally a few other compounds which include the only hetrocompound identified (dibenzofuran). It should be noted that biphenyl was one of the most abundant compounds. A total of 18 identified compounds appear on this list and 28 other isomers were separated and partially identified.

This presentation demonstrates the potential application of computerized GC-MS systems to environmental problems involving complex hydrocarbon mixtures. It contains several shortcomings. The chromatograms for the figures, for instance, were derived from packed Apiezon L columns, while they should have been recorded from the same columns used to derive the mass spectra. Ideally, the retention data should be stored in the computer and used as complementary information for the computer assisted interpretation of mass spectra [5]. Identifications have been made by extensive use of computer derived mass chromatograms [6] and manual interpretation and thus have been too time consuming. Future plans include computer mass spectral matching and quantitative estimation by GC methods. It is considered that the shortcomings can all be resolved and that the kind of information mentioned at the beginning of this paper will be forthcoming with sufficient time and effort.

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TABLE III.

INDANES, BIPHENYLS, AND OTHER ORGANICS FOUND IN A METHYLENECHLORIDE EXTRACT OF AN ESTUARINE WATER ACCOMMODATE OF A NO. 2 FUEL OIL BY GC-MS

INDANES, C_9 to C_{11}

b INDANE, C_9H_{10} T
1- METHYLINDANE
2- METHYLINDANE

ISOMERS SEPARATED, NOT SPECIFICALLY IDENTIFIED

		NO.
c	METHYLINDANES	2
	ETHYLINDANE	1
	DIMETHYLINDANES	6

BIPHENYLS, C_{12} to C_{15}

a BIPHENYL, $C_{12}H_{10}$ M
b 2 - METHYLBIPHENYL
3 - METHYLBIPHENYL
4 - METHYLBIPHENYL

ISOMERS SEPARATED, NOT SPECIFICALLY IDENTIFIED

		NO.
c	DIMETHYLBIPHENYLS	3
	C_2-SUBST'D BIPHENYLS	2
	C_3-SUBST'D BIPHENYLS	3

HIGHER CONDENSED RING HYDROCARBONS, C_{12} to C_{15}

a ACENAPHTHENE $C_{12}H_{10}$
FLUORENE, $C_{13}H_{10}$
ANTHRACENE, $C_{14}H_{10}$

ISOMERS SEPARATED, NOT SPECIFICALLY IDENTIFIED

		NO.
c	METHYLFLUORENES	4
	C_2-SUBST'D FLUORENES	3
	METHYLANTHRACENES	4

SATURATED ALIPHATIC HYDROCARBONS, C_{10} to C_{13}

a n - DECANE, $C_{10}H_{22}$
n - UNDECANE, $C_{11}H_{24}$
n - DODECANE, $C_{12}H_{26}$
b n - TRIDECANE, $C_{13}H_{28}$

OTHER ORGANICS, C_{12} to C_{14}

a DIBENZOFURAN, $C_{12}H_8O$
DIPHENYLMETHANE, $C_{13}H_{12}$
c PHENYLCYCLOHEXANE, $C_{12}H_{16}$
1,1 - DIPHENYLETHENE, $C_{14}H_{12}$ T

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Key Words: Computer, Fossil hydrocarbons, No. 2 fuel oil, Gas chromatograms, Mass spectrometry, Specific compound identification, Water accommodate.

TOPICAL SESSION III.

Standards and Intercomparison Criteria

NBS Spec. Publ. 409, Marine Pollution Monitoring (Petroleum), Proceedings of a Symposium and Workshop held at NBS, Gaithersburg, Maryland, May 13-17, 1974 (Issued December 1974).

THE ROLE OF STANDARD REFERENCE MATERIALS IN ENVIRONMENTAL MONITORING

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This paper describes meaningful measurements and how they are obtained; some of the factors that go into making a meaningful measurement; and the role that NBS-Standard Reference Materials (SRM's) play in that effort. In addition, the philosophy of certification of NBS-SRM's is given followed by a short description of currently available and planned NBS environmental SRM's, and the possibility of NBS producing trace crude oil constituent SRM's.

The goal in any measurement is to produce meaningful data - - for data to be meaningful it should be accurate, precise, and specific. Figure 1 has been used with some success as an analogy to explain the difference between accuracy and precision: Three imaginary marksmen fire a rifle at a target. In the top target, the marksman is both imprecise and inaccurate. The marksman is quite precise but inaccurate in the middle target, and in the bottom target, the marksman is both accurate and precise. Of course, the analogy in all cases is that the bull's eye corresponds to the target value or "true" value.

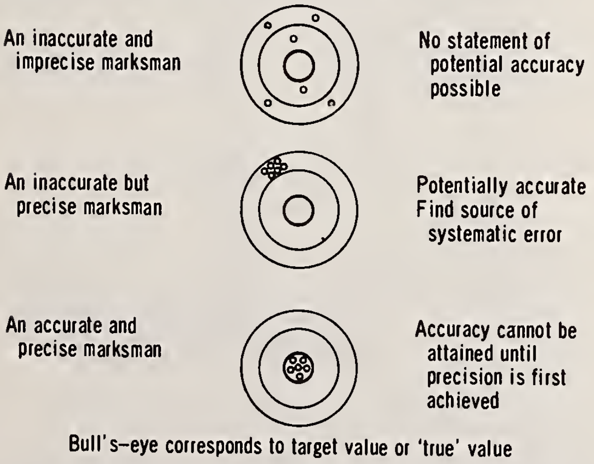

Figure 1. Accuracy and Precision

Turning to specificity, the determination of strontium in granite done at NBS several years ago is an interesting example of the meaning of specificity. The results obtained by two different methods are shown in figure 2: 1.0 ppm Sr obtained by atomic absorption with a standard deviation of ±10 percent; and 17.0 ppm Sr obtained by neutron activation analysis with a standard deviation of ±5 percent. Which result is closer to the bull's eye? In this case, the atomic absorption results were more accurate even though they had a standard deviation twice that of the neutron activation analysis measurements.

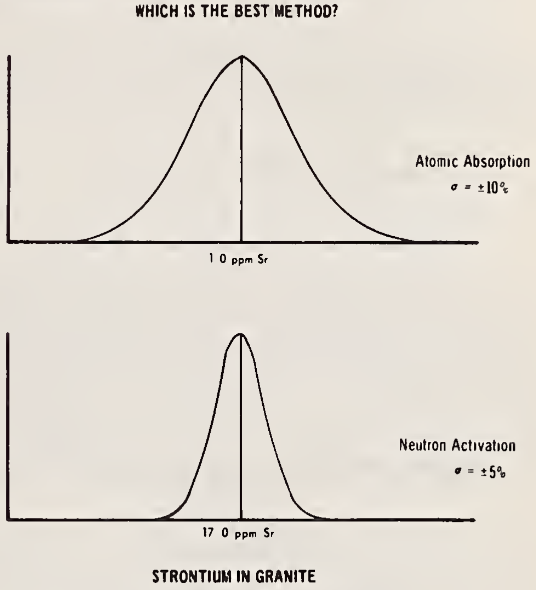

Figure 2. Strontium in Granite

The reason for the larger error in the neutron activation analysis results was, non-specificity of the technique. The granite besides containing Sr, also contained uranium-235 which fissioned on irradiation with neutrons to give an additional apparent 16 ppm Sr, as shown by figure 3.

NBS-SRM's are designed to be tools to help insure meaningful measurement. An NBS-SRM is defined as a well-characterized material, produced in quantity and certified by NBS to help: calibrate instruments, develop reference methods of measurement, and provide long-term quality control in a measurement system. It should be noted that NBS has a congressional mandate to provide nationally authoritative SRM's.

One of the most important facts built into most NBS-SRM's is known accuracy. The accuracy of an NBS-SRM is generally established by one or more of three routes to certification. These three routes are arranged in order of preference and are:

SYSTEMATIC ERROR - THE VILLAIN

The Strontium contained in the granite is made radioactive by irradiation with neutrons and the radioactive Sr is then counted and the original Sr content calculated: Thus:

$$^{88}\mathrm{Sr} + \mathrm{n} \longrightarrow {}^{89}\mathrm{Sr} \xrightarrow[54\mathrm{d}]{\beta} {}^{89}\mathrm{Y}\ \text{(stable)}$$

BUT (the villain) granite contains uranium and

$$^{235}\mathrm{U} + \mathrm{n} \xrightarrow[\text{products}]{\text{fission}} {}^{89}\mathrm{Sr} \xrightarrow[54\mathrm{d}]{\beta} {}^{89}\mathrm{Y}\ \text{(stable)}$$

And there is no physical way of differentiating the ^{89}Sr formed from the uranium from that formed from the natural occurring strontium.

1 ppm U gives an apparent 16 ppm Sr

Figure 3. Systematic Error

refererence method, two independent methods, or round robin tests. The preferred route to certification is by a reference method, which is a method of known or proven accuracy. Its use assures the accuracy of the determination if personal bias is eliminated. This is eliminated by having the measurements made, when possible, by two or more analysts.

The second route to certification is used when a reference method is not available. The route requires the use of two or more independent methods. Each of these independent methods must have estimated systematic biases that are small relative to the accuracy goal set for certification.

The first two routes are subject to critical scientific review through statistical analysis of the data obtained. This, however, may not be the case for the third or round robin route, which may be subject to a somewhat less rigorous analysis of the data. The case can be made that this route is valid because in a system under good quality control, (based on accuracy) it works.

The following examples illustrate the certification of NBS-SRM's using each of these three routes. NBS has issued a series of glass SRM's certified for trace elements at levels from 0.02 to 500 ppm. The lead content of these SRM's was certified using isotope dilution thermal ion source mass spectrometry, which is a recognized method of known and proven accuracy for lead. Similar standard deviations were obtained using this method by two analysts working 2,000 miles apart, (fig. 4). These results are important as they signify that the system was under control. The certified value of 426 ± 1 ppm for lead is a conservative figure that provides for possible unknown sources of systematic error.

LEAD IN 500 PPM GLASS

Rod No.	Analyst 1	Analyst 2
2	426.5	- - -
13	426.2	- - -
18	425.6	425.9
48	426.1	426.0
56	426.9	425.0
66	426.0	425.4
78	426.2	425.6
106	425.7	- - -
Average	426.15	425.58
σ	±0.41	±0.40

Figure 4. Lead in Glass SRM

As an example of the second route, three independent methods of analysis were used to determine cadmium in SRM 1577, Bovine Liver. Isotope dilution spark source mass spectrometry, atomic absorption, and polarography gave 0.28, 0.27 and 0.25 ppm, respectively, with the certified value being at 0.27 ± .04, (fig. 5).

CERTIFICATION BY TWO OR MORE INDEPENDENT METHODS

Cadmium in Bovine Liver

	Concentration (μg/g)		
Sample	ID–MS	Atomic Absorpt	Polarography
1	0.32 0.29	0.29	– –
2	0.26 0.27	0.24 0.26	0.26
3	0.27 0.27	0.26 0.27	0.16*
4	0.28	0.24 0.27	0.28
5	– –	0.30	0.28
6	0.26	0.26	– –
$\bar{X}$	0.28	0.27	0.25
2σ	0.04	0.04	0.11

Range (all results) 0.24 – 0.32

Recommended Value 0.27 ± 0.04

Figure 5. Cadmium in Liver SRM

In this case it is not a reference method as was the case for lead because the systematic errors have not be exhaustively studied for Cd. The third route to certification, interlaboratory testing, is shown in figure 6. This round robin involved six different, highly competent

CERTIFICATION BY CONSENSUS
SRM 337 – Basic Open-Hearth Steel
Carbon

ANALYST	METHOD/VARIATION (Note: Combustion step common to all)	% CARBON
1	Gravimetric – 1 g sample	1.08
2	Gravimetric – 3 g sample	1.06
2	Volumetric – 1 g sample	1.06
3	Gravimetric – Factor weight (2.73 g) sample	1.06
3	Gasometric – 1 g sample	1.07
4	Gravimetric – Half-factor weight (1.36 g) sample	1.06
5	Gravimetric – Half-factor weight (1.36 g) sample	1.08
5	Thermal Conductivity 0.7 g sample	1.08
6	Gravimetric – 0.7 g sample	1.07

Mean 1.07

Figure 6. Carbon in Steel SRM

laboratories in the determination of the carbon content of a steel SRM. Although four different methods and six different sample weights were used, highly satisfactory results were obtained. It should be noted, however, that a previously issued NBS-SRM, similar to the material under study, was required for internal quality control in each of the laboratories. The use of the round robin approach should only be used for measurement systems or fields of science and technology that have already obtained good quality control. Several reasons exist for avoiding the round robin approach. First, a field may not be ready for it, as the field is not in good quality control. Secondly, that the proper constraints, i.e., sampling procedures, statistical interpretation of the data, etc., may not be rigorously applied. An illustration of the danger in the round robin approach can be seen (fig. 7) from the wide range of values reported by different laboratories for various elements in this orchard leaves SRM. These data could not be used for certification! This SRM was actually certified for some 14 different elements using the second route.

CERTIFICATION BY CONSENSUS
A DANGER
Orchard Leaves

Element Determined	No. of Labs	Mean $\bar{X}$	Range	$S/\bar{X}$ %
P	10	0.20%	0.14 – 0.24	25
Al	10	222 μg/g	99 – 401	36
Fe	11	239 μg/g	151 – 367	28
Mo	5	5.4 μg/g	2.3 – 10.5	59

Figure 7. Orchard Leaves SRM

An important segment of the U.S. measurement system, is dependent on SRM's. For SRM's to be most effective, they need to be integrated in this or a similar system. Figure 8 shows the parts of the U.S. measurement system and how they tie the first link in this measurement system, and form the common foundation for all quantitative measurement systems. Fortunately, these units have been agreed upon internationally, and are called SI units from the Systéme International de Unités (International System of Units). Producing and distributing certified SRM's on a national basis is the next link to the measurement chain. In the U.S., this is mainly the job of NBS, as has been prescribed by congressional legislation. Other organizations produce calibration materials in their particular field of science or technology. An example of this is the U.S. Geological Survey, which produces geological samples. The next link in this system is reference methodology. A reference method of measurement is defined at NBS as a method of known and demonstrated accuracy. In addition, the accuracy inherent in the method has been shown to be transferable by interlaboratory testing.

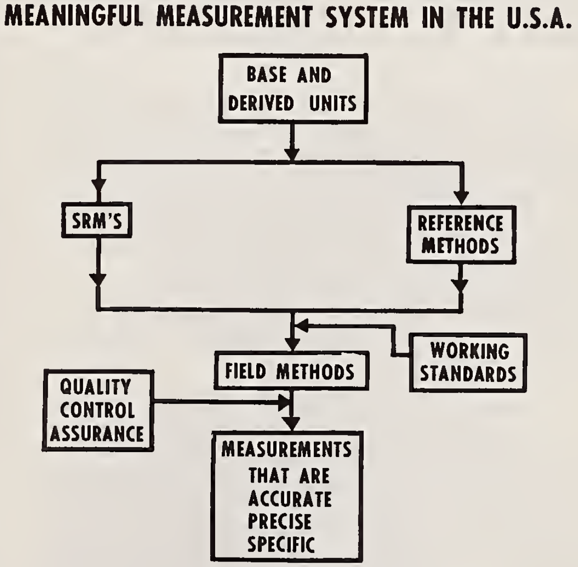

Figure 8. U.S. Meaningful Measurement System

The base and derived units and SRM's are the direct responsibility of NBS. This is not the case for reference methods. NBS becomes involved in reference methods only when outside organizations have not or cannot develop reference methods by themselves. However, many collaborative efforts do exist between NBS and professional societies, standards bodies, trade associations, and other Government agencies to provide SRM's and reference methods. An example of NBS involvement in such work is the development of a reference method for the determination of calcium in serum [1].

Primary SRM's and reference methods do not find wide-spread daily use in measurement laboratories. But they tie directly to the next link in the system - - the field methods of test and working or everyday calibration standards. When used together, reference methods and NBS-SRM's provide organizations with the means to evaluate their working standards and field methods of test. As a consequence they allow measurements to be based on accuracy.

From this network, measurements are produced that are meaningful in terms of accuracy and precision. One more part is needed to insure that the system works smoothly and produces the desired results over a long period of time. A quality control assurance program involving interlaboratory testing with unknown samples and analysis of the results as evaluated against SRM's and reference methods fulfills this need. Quality control assurance programs are sponsored in the U.S. by many different organizations. However, they are not always based on SRM's and reference methods. As a result, some of these quality assurance programs give a measure of between-laboratory precision only.

The description of how NBS-SRM's are certified and how they fit into the measurement system provides a suitable introduction to a group of NBS-SRM's specifically designed to meet the somewhat lengthy measurement-needs for environmental work. What environmental SRM's are currently available from NBS? The complete list of currently available environmental SRM's is given in the SRM Catalog [2] which can be obtained from NBS free-of-charge.

Gaseous SRM's in stock include propane, carbon monoxide, and carbon dioxide for engine exhaust monitoring and standard air certified for oxygen content. The standard air is used to monitor long-term oxygen trends in the atmosphere and to detect any changes in the air's oxygen content. In addition, sulfur dioxide permeation tubes are available that have been certified for their SO_2 permeation rate.

In the fuels area we have residual and distillate fuel oils and coal certified for their sulfur content at several concentrations. Thus, the problem of SO_2 levels in the air is addressed from two points; before burning (fuels) and afterward (permeation tubes).

Another coal SRM is certified for trace concentrations of mercury; while two biological SRM's, orchard leaves and bovine liver, are certified for trace amounts of toxic heavy metals. And finally, a large number of radioactive SRM's are available for monitoring the air, water, and solids around nuclear power plants and fuel reprocessing facilities.

The following SRM's are now in the development or production stages at NBS: urban air particulate (heavy metals); lead in gasoline; mercury in water; mercury in tuna fish; river sediment (radioactivity); NO_2 permeation tube; nitric oxide in nitrogen; coal, fly ash, and fuel oil (trace elements).

What environmental SRM's are planned for the future? Specifically, what about NBS-SRM's certified for trace amounts of the constituents of crude oil? Hopefully, the needs for these SRM's can be well defined in terms of which crude oil constituents, at what concentrations in which natural matrices are needed. Obviously, since SRM's cannot be made for every possible combination, the problem must be approached by developing several "bench mark" SRM's that can be used to tie the field together. For example, one could envision a biological material set of SRM's, a botanical materials set of SRM's, a sediment or soil set of SRM's and perhaps an aqueous set of SRM's. Each of the same material with several concentration levels for one or more crude oil constituents. Of course, the stability, size, and number of each SRM to prepare based on expected sales are questions that also need to be answered before NBS can begin to produce these SRM's. The need for SRM's in the whole area of water pollution is considered to be extremely important. NBS is currently surveying the field with a questionnaire to determine which SRM's have the highest priority.

References:

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[2] Office of Standard Reference Materials, Standard Reference Materials: 1973 Catalog, NBS Spec. Publ. 260, U.S. Government Printing Office, Washington, D.C. 20402 (1973).

Key Words: Accuracy; environmental monitoring; marine pollution; NBS-Standard Reference Materials; water pollution.

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STANDARD AND INTERCOMPARISON CRITERIA: TAR BALLS AND PARTICULATE MATTER

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The study of tar balls and particulate matter is important in determining the fate of petroleum in the marine environment. Ideally, scientists interested in various aspects of petroleum pollution should be able to rely on published data for comparison of results. Unfortunately, one cannot make comparisons with certainty, because the results from even the same sample may vary according to the analytical procedure used.

Appropriate standards and blanks are basic to good experimental design, but the need for intercomparison of analytical procedures has not been so readily recognized. The feasibility of intercomparison standards has been recently demonstrated by Farrington et al (1). In addition to the use of intercomparison standards, it would be desirable to devise guidelines to help standardize analytical procedures and to limit the number of different techniques.

We are involved in a study of the fate of a #6 fuel oil spilled in Narragansett Bay, R.I. Certain aspects of our study may be used to exemplify the need for adequate standards and intercomparison procedures.

The adequacy of the analytical procedure to follow changes in the aliphatic and aromatic hydrocarbon fractions of the spilled oil was determined by carrying various standard hydrocarbons through the extraction, clean-up, fractionation and analysis procedure. A series of n-alkanes, branched and cyclic aliphatic hydrocarbons and aromatic hydrocarbons were tested. A wide variety of compounds was used to detect differential recoveries of the various petroleum components due to differences in solubility and volatility.

Along with quantifying the recovery of standards, blanks are especially important when analyzing particulate matter. The low concentration of petroleum associated with particulate matter requires very high concentration factors which greatly magnify contaminants.

To determine how the results from our analytical procedure compared with others, a sample of the #6 fuel oil was sent to Dr. James G. Quinn at the University of Rhode Island, Graduate School of Oceanography. A comparison of our analysis of the #6 fuel oil (fig. 1) with that of Quinn and Wade (Unpublished Data) (fig. 2) shows how different analytical procedures may produce dissimilar chromatograms for the sample (The predominent peaks in fig. 2 corresponding to 190 °C and 220 °C are internal standard hydrocarbons n-C_{22} and phenanthrene).

A tar ball resulting from the oil spill (fig. 3) was analyzed in our laboratory for comparison with the #6 fuel oil data. Using our data (fig. 1) we can identify the #6 fuel oil as the source of the tar ball with considerable certainty, however, we could not make the identity by comparing

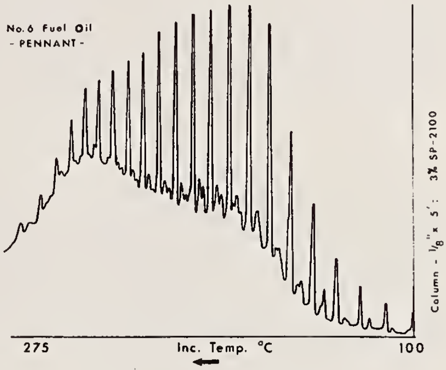

Figure 1

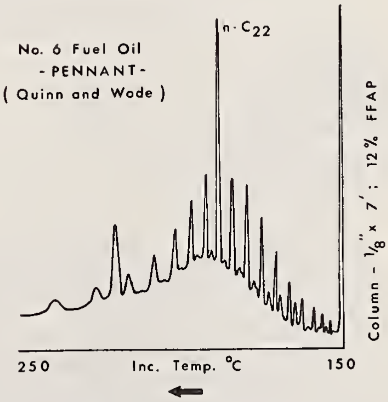

Figure 2

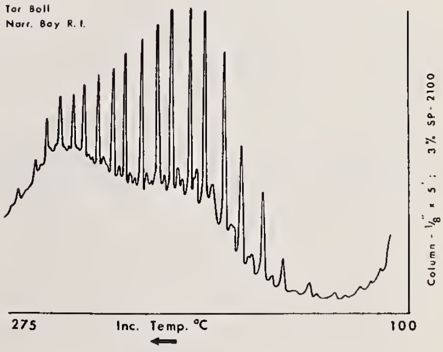

Figure 3

our tar ball chromatogram with the #6 fuel oil chromatogram of Quinn and Wade (fig. 2).

The difference in the results of the #6 fuel oil analyses was due primarily to different conditions during GC analysis. The procedure of Quinn and Wade included TLC to separate the aliphatic and aromatic hydrocarbon fractions (Table I) and GC analysis using a column of 12% FFAP on 80/100 mesh Chromosorb WHP, temperature programmed from 150 °C to 250 °C at 8 °/min. Our procedure used column chromatography for separation of these components (Table I) and GC analysis with a column of 3% SP-2100 on 100/120 Supelcoport, temperature programmed from 100 to 275 °C at 6 °/min. A column of 12% FFAP was also used in our procedure to provide a separation of n-alkane and isoprenoid hydrocarbons.

Although the chromatograms show dissimilar patterns under these different GC analytical procedures, a more involved comparison of select characteristics of the chromatograms provided a good correlation of our results with Quinn and Wade (Table I). Thus it is possible to correlate data obtained by different methods if it is known how the analytical procedures compare.

Table I. A Comparison of Results from Different Analyses of a #6 Fuel Oil.

	Pierce & Traxler	Quinn & Wade
% Aliphatic	87^a	89^b
% Aromatic	13^a	11^b
n-C_{17}/pristane	1.8^b	1.8^b
pristane/phytane	1.0^b	1.0^b

a Column = 3% SP-2100
b Column = 12% FFAP

Pierce et al (2) suggested that particulates provide a means for hydrocarbon transport and incorporation into the food chain. The analysis of petroleum associated with particulate matter requires a more intricate approach than for tar balls, due to the low concentration of petroleum and the abundance of non-petroleum hydrocarbons. Often the presence of petroleum may be masked by the abundance of non-petroleum hydrocarbons.

A useful approach to this problem would be to determine the natural background of hydrocarbons before petroleum is introduced to the environment. Baseline surveys are important for areas where oil drilling and transport may occur in the future.

Instrumentation required for a complete analysis of petroleum is beyond the capability of most laboratories. The asphaltic fraction, which may be the most critical portion of petroleum concerning toxicity, carcinogenicity and persistence, cannot be analyzed by GC. More emphasis is needed on high speed liquid chromatography and various detection and data retrieval systems for the asphaltic fraction, such as those discussed by Gruenfeld (3).

Solving problems of petroleum pollution requires input from studies utilizing relatively simple techniques as well as extremely sophisticated instrumentation. The exact procedure used is not as important as knowing how the procedure compares with others and recognizing the limitations.

To allow for proper intercomparison of data, it is essential to agree on certain guidelines to follow during petroleum analysis.

In general, the purpose for standards and intercomparison is to determine the adequacy of an analytical procedure and the certainty with which results from different analyses may be compared. From this discussion, some obvious criteria for standards and intercomparison procedures emerge: detect petroleum over natural background; determine percent recovery and reproducibility; quantitate petroleum fractions and compounds; quantitate sample loss and contamination.

Recognizing what is required of standards and intercomparison procedures, we may suggest guidelines for obtaining this information: intercomparison with a standard petroleum fraction mixed with a recently biosynthesized oil; analysis of "standard" particulate matter; internal standards with each sample; blanks with each set of sample analyses.

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Key Words: Standards and intercomparison criteria; Tar balls, Particulate matter; Petroleum analysis, Gas chromatography.

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ANALYSES OF HYDROCARBONS IN MARINE ORGANISMS: RESULTS OF IDOE INTERCALIBRATION EXERCISES

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Introduction

The importance of intercalibration of hydrocarbon analyses between laboratories was recognized early in the program of baseline studies of the Office for the International Decade of Ocean Exploration, National Science Foundation. Three participating laboratories analyzed a cod liver sample spiked with a distillate cut of South Louisiana crude oil. The results of this exercise have been published [1].

Four participating laboratories analyzed a tuna meal sample provided as a working intercalibration sample through the courtesy of the National Bureau of Standards. The methods of analysis were not specified. Each laboratory analyzed the sample using the techniques and methods employed at that time in the respective laboratories. Our methods of analysis limit us to hydrocarbons of molecular weights in the range of n-C_{14} to n-C_{33} and as such we refer only to this range when speaking of "hydrocarbons" or "total hydrocarbons" in general terms.

Methods of Analysis

The limited space allowed in this presentation permits only a brief outline of the methods of analysis. A more detailed description is available [2, 3].

Laboratories A and D weighed fractions of the concentrate of column chromatography eluates on a Cahn electrobalance to obtain weights of hydrocarbons in each fraction. Laboratories A, C and D used an external standard analyzed with the same instrument conditions as for sample analysis to calibrate the FID of the gas chromatographs. Laboratory B used an internal standard n-C_{22} spiked to one subsample of tuna meal to calibrate the FID. Peak areas were measured by the method of peak height x width at one half height. The unresolved complex mixture area of the chromatogram was determined by planimetry.

Results and Discussion

The concentrations of resolved or partially resolved peaks, unresolved complex mixture, and total hydrocarbons are given in Table I. The unresolved complex mixture concentration was not a routine measurement in one laboratory and was not reported from that laboratory.

We think that the agreement between all laboratories for the measurement of the resolved and partially resolved components is as good as can be expected considering that no method of analysis was specified. This is especially so if one takes into account the fact that squalene was present in the tuna meal sample. The squalene would be only partially recovered in the hydrocarbon fractions in some chromatography operations, while in other cases squalene would be present in two or more fractions from chromatographic separation of hydrocarbons. In addition, squalene is very labile.

We have corrected the values for the resolved peaks by subtracting the concentration values for squalene. We have assumed in doing this that the major peak with retention index similar to that of squalene is in fact squalene. The corrected concentration values are presented in Table II. The agreement between laboratories for the resolved or partially resolved component concentrations is improved. Since squalene is a major component in most fish and shark liver samples, the problems we have encountered here with squalene would also occur in analyzing fish and shark samples and probably also with other biological samples.

The agreement between laboratories for the unresolved complex mixture concentration is fair e.g. compare total of A1 + A2; A3; B_1, B_2; total of D1 + D2 + D3. The unresolved complex mixture of hydrocarbons is used as an indication of petroleum hydrocarbons in some laboratories for screening samples to detect petroleum hydrocarbons [1,4].

The total hydrocarbon concentrations as determined by weighing are also given in Table I. A comparison of the totals obtained by weighing and the totals obtained by GC analysis show the former to be higher in all but one case. We think this is the result of the presence in the tuna meal of hydrocarbons with molecular weight greater than the 33 carbon n-alkane. These hydrocarbons would be weighed but would not be measured by the GC analysis employed because they would not have eluted from the column during the time of analysis. This same phenomena has been observed for the analysis of sediment samples and for the analysis of some fish tissue and fish liver samples [5].

OUTLINE OF METHODS

Laboratory	Extraction Method	Method of Separation of Hydrocarbons
A	Soxhlet extraction with MeOH 48 hours: saponification of lipids for one subsample	Column chromatography on Al_2O_3 (5% H_2O) over SiO_2 (5% H_2O)
B	Reflux extraction with benzene: MeOH (2:1) saponification of lipids	Thin layer chromatography on Silica Gel G.
C	Soxhlet extraction with MeOH followed by hexane: benzene (9:1): saponification of lipids	Column chromatography on Al_2O_3 (6% H_2O) over SiO_2 (5% H_2O)
D	Soxhlet extraction with MeOH 24 hours: saponification of lipids	Column chromatography on Al_2O_3 (5% H_2O) over SiO_2 (5% H_2O)

Gas chromatographic analyses were as follows:

Laboratory	Column	Temperature Program
A	a. 2.34 m x 3.2 mm o.d. 3% ApL on Chrom. W 80/100	80° to 290°C at 6°/min.: held at 290°C until n-C_{28} eluted
	b. 3.1 m x 3.2 mm o.d. 12% FFAP on Chrom. W 80/100	125° to 270°C at 4°/min.: held at 270°C until n-C_{28} eluted
B	1.8 m x 3.2 mm o.d. 3% ApL on Chrom. W 80/100	150° to 280°C at 6°/min.: held at 280°C until n-C_{28} eluted
C	a. 2.13 m x 3.2 mm o.d. 5% FFAP on Gas Chrom. Q	100° to 285° at 6°/min.
	b. ApL SCOT column 45.7 m	120°Cto 225°C at 4°/min.
D	2.34 m x 3.2 mm o.d. 3% ApL on Chrom. W 80/100	80° to 290°C at 6°/min. held at 290°C until n-C_{28} eluted

A comparison of the reported relative abundance of n-alkanes to pristane for the four laboratories is given in Table III. The agreement is fair overall with a few discrepancies. It is interesting to note that the discrepancies are not always from the same laboratory. The result for the analysis of the n-alkanes are somewhat disappointing given the agreement for pristane concentrations in cod liver oil which was analyzed by three laboratories[1].The concentration values for the pristane in tuna meal are given in Table IV. The agreement for pristane at the 1 to 10 μg/g dry weight level is not as good as that achieved for the cod liver sample at the 200 to 300 μg/g lipid concentration level for pristane. We estimate on the basis of lipid analysis that tuna meal contains 15 to 50 μg pristane/g lipid. The precision for the tuna meal pristane concentration is ±64% relative standard deviation compared to the precision of ±2% r.s.d. for the pristane in the cod liver oil.

Table I. Hydrocarbons in Tuna Meal (μg/g dry weight)

	A1	A2	Total	A3	B_1	B_2	C	D1	D2	D3	Total
Resolved Peaks	8.5	23.0	31.5	12	18.0	20.2	26.0	7.5	NA	50.0	57.5
Unresolved Complex Mixture	39.0	10.0	49.0	41	29.5	35.2	ND	39.7	NA	NP	39.7
Total (g.c.)	47.5	33.0	80.5	53	47.5	55.4	-	47.2	NA	50.0	97.2
Total (weighing)	106.0	76.5	182.0	140	NA	NA	-	57.2	13.6	50.0	120.5

Laboratory A - Column Chromatography -
A1: 2 column volumes of pentane; A2: 2 column volumes benzene; A3: 3 columns of 5% benzene in pentane.
Laboratory B - B_1, B_2 duplicate analyses TLC procedure.
Laboratory C - Colum Chromatography - 1 column volume hexane.
Laboratory D - Column Chromatography -
D1: 1 column volume pentane; D2: 1 column volume 10% benzene in pentane; D3: 1 column volume 20% benzene in pentane.

NA - Not analyzed
NP - Not present

Table II. Hydrocarbons in Tuna Meal Corrected by Deduction of Squalene Concentration (μg/g dry weight)

	A1	A2	Total	A3	B_1	B_2	C	D1	D2	D3	Total
Resolved Peaks	8.5	10.4	18.9	8.5	12.4	13.1	26.0	7.5	NA	13.8	21.3
Unresolved Mixture	39.0	10.0	49.0	41.0	29.5	35.2	NA	39.7	NA	NP	39.7
Total	47.5	20.4	67.9	49.5	41.9	48.3	-	47.2	13.6	13.8	74.6

NA - Not analyzed
NP - Not present

Table III. Abundance of n-Alkanes Relative to Pristane

n-Alkane	A-1	A-3	B	C	D
15	0.81	0.85	N.R.	0.66	0.67
16	0.12	0.09	0.40	0.13	0.04
17	0.40	0.42	0.40	0.39	0.44
18	0.17	0.17	0.17	0.09	0.14
19	0.17	0.15	0.17	0.20	0.03
20	0.13	0.11	0.10	N.R.	0.05
21	0.17	0.14	0.14	0.06	0.17
22	0.12	0.45	0.27	N.R.	0.04
23	0.13	T	N.R.	N.R.	0.16
24	0.13	T	N.R.	0.01	0.04
25	0.07	N.R.	N.R.	N.R.	0.03
26	0.11	N.R.	0.40	N.R.	0.06
27	0.12	N.R.	N.R.	0.07	0.05
28	0.12	N.R.	N.R.	N.R.	N.R.

NR - Not reported
T - Trace

Table IV. Pristane Concentration in Tuna Meal (μg/g dry weight)

A1	A3	B	C	D
1.9	2.0	3.0	5.7	2.0

We believe that the latter value is fortuitous and does not reflect the true precision of the analysis since the best precision one would expect for measurement of the GC peak for pristane is about ±5% r.s.d.

The results we report here are only a start at intercalibration of analyses for hydrocarbons in marine tissue samples. The need for intercalibration of much more sophisticated techniques such as GC-mass spectrometry and compound type analyses by mass spectrometer-computer systems is already apparent as these techniques are now being used for analysis of hydrocarbons isolated from marine samples.

There has been an increase during the last few years in the number of laboratories analyzing marine samples for hydrocarbons and attempting to determine petroleum hydrocarbons in the presence of recently biosynthesized hydrocarbons. Our experience reported here and elsewhere, [1] points to the need for intercalibration. Our laboratories now have a basis for comparing results of analyses of marine tissue samples. We think it is absolutely essential that intercalibration be expended to include more laboratories, more analytical methods and different types of samples. We also think that there is an obvious need for intercalibrations where the same methods of analysis are used.

Acknowledgements:

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Key Words: Hydrocarbons in Marine Organisms; Intercalibration; Oil Pollution.

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IDOE-5 INTERCALIBRATION SAMPLE: RESULTS OF ANALYSIS AFTER SIXTEEN MONTHS STORAGE

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Introduction

The advent of growing scientific and governmental interest in marine oil pollution has heightened the need to intercalibrate the various analytical techniques employed in oil pollution study. Laboratories engaged in the quantification of petroleum hydrocarbons require intercalibration to facilitate comparison of data and to assess the precision and accuracy of their methods of analysis. For initial intercalibration efforts of this type, chemically stable, petroleum-spiked samples are needed.

We participated with two other laboratories in an intercalibration exercise in 1972 (1) using as an intercalibration sample a cod liver lipid extract spiked with a distillate cut of South Louisiana crude oil. In order to test the stability of this sample, we withdrew two subsamples and stored them separately from the bulk mixture. We have analyzed these subsamples sixteen months later using the techniques detailed below. These techniques are slightly modified from the original techniques employed by our laboratory in the earlier study (1). The gas chromatography (GC) screening procedure and its application to the study of petroleum pollution in marine samples have been discussed elsewhere (1, 2, 3).

Experimental

Preparation of IDOE-5 Intercalibration Sample

A cod liver lipid extract was spiked with 371.8 μg of a distillate cut (n-C_{16} to n-C_{28}) of South Louisiana crude oil per gram of lipid in January, 1972. The sample was stored under N_2 at 0°C in the dark in a glass bottle with a Teflon lined cap. The subsamples were withdrawn from the bulk mixture on August 16, 1972 and October 22, 1972 after warming the mixture to room temperature and allowing the lipids precipitated from the sample at 0°C to go into solution. The subsamples and the main sample were then flushed with nitrogen and stored at 0°C in the dark in glass bottles or vials with Teflon liners.

Methods of Analysis

In February, 1974, lipid concentrations of each subsample were determined and aliquots containing about 120 mg of lipid were saponified under reflux for twenty-four hours in 0.3 N KOH in 3:1 methanol:water solution. Non-saponifiable lipids were partitioned from the aqueous methanol solution into pentane, and the pentane extracts were dried by standing at least two hours over Na_2SO_4. The extracts were evaporated to dryness and the resulting residues were weighed.

Residues were dissolved in 1 ml of pentane and charged to columns of 4 g alumina (5% water) packed over 4 g silica (5% water). The columns were eluted with one column volume each of pentane, 10% benzene in pentane, 20% benzene in pentane, and benzene. The second and third eluates were combined for subsequent analysis.

Quantification of hydrocarbons was accomplished by the following GC method. Chromatograms of the first eluate and the combined second and third eluates were obtained on a 5 ft. x 1/8 in. OV 101 on 100/120 mesh H/P Chromosorb column. The column was operated with a He carrier gas flow rate of 10 to 15 ml/min., and temperature was programmed from 70 to 270°C at 6°C per minute. The instrument employed was a Varian 1400 GC equipped with a flame ionization detector. The detector signal was routinely calibrated for sample experimental conditions by obtaining a chromatogram of a standard mixture of n-alkanes n-C_{14} to n-C_{28} (even carbon numbers). Peak areas on sample and standard chromatograms were calculated using peak height times peak width at half height. The unresolved complex mixture area in the sample chromatograms was determined by planimetry. The integrated area of the unresolved complex mixture and the peaks other than pristane is used as the estimate of petroleum hydrocarbons in the sample (1, 3).

Results and Discussion

The results of our recent analyses and the average values obtained 18 months earlier are presented in Table I. They are in agreement

Table I. μg Hydrocarbons /g Cod Liver Lipid.

	Ave. Value ± s.d.(1972)	8/16/72	10/22/72
Peaks and Complex[a] Mixture (pet.hyd.)	406 ± 26 μg/g	455 μg/g	426 μg/g
Peaks	79.2 ± 10.5	71	59
Complex Mixture	326.8 ± 27.7	384	367
Pristane	270.4 ± 5.2	267	270

This is used as the estimate of petroleum hydrocarbons and includes peaks other than pristane.

within interlaboratory and intralaboratory precision for this type of analysis. Figure 1 contains chromatograms of (1) the distillate cut, (2) pentane-eluted hydrocarbons in unspiked cod liver lipids, (3) pentane-eluted hydrocarbons in the original intercalibration exercise and, (4) pentane-eluted hydrocarbons in our recent analyses. The chromatograms from the original exercise were obtained on a 7.5 ft. 1/8 in. Apiezon L column. Although the two IDOE-5 chromatograms shown in Figure 1 were obtained on two different GC columns, the results are comparable for the purposes of this type of analysis.

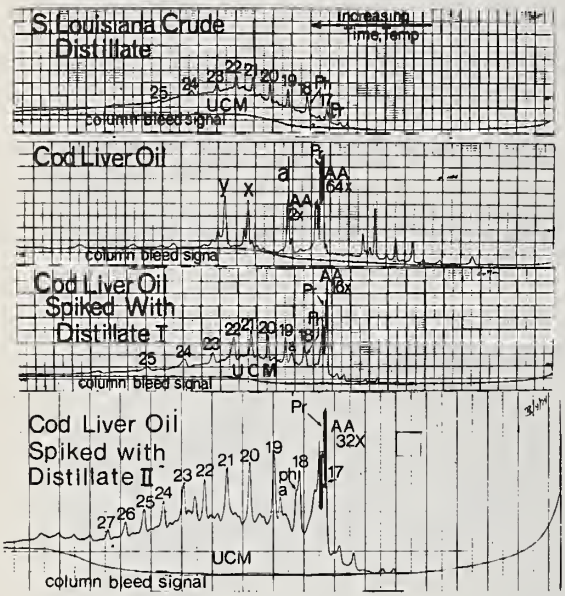

Figure 1.
Gas chromatograms of hydrocarbons in pentane eluate of column chromatography.

AA - Automatic attenuation of detector signal
UCM - Unresolved complex mixture
Pr - Pristane
Ph - Phytane
Numbers - n-alkanes

I - Chromatogram obtained in original intercalibration on 3% Apiezon L. column.

II- Chromatogram obtained in recent analyses on 1.5% OV-101 column.

The major portion of the petroleum distillate cut spiked into the cod liver lipid elutes from column chromatography in the first fraction (pentane eluate). A small portion elutes in the second fraction (10 and 20% benzene) and none is detected in the third fraction (benzene eluate). This is not to be expected for all crude oils, fuel oils or other petroleum products and should be considered characteristic only for this distillate cut. A comparison of the unresolved complex mixture values for Fractions I and II and the values for the analysis of the petroleum distillate cut by column chromatography are given in Table II.

Table II. Hydrocarbons from Petroleum Distillate Cut in Column Chromatography Fractions.

	IDOE-5 8/16/72	10/22/72	S.Louisiana Crude Distillate Cut
Fraction I	90%	85%	85%
Fraction II	10%	15%	15%

The comparison shows that the values are in general agreement although the data is insufficient at this time to provide an estimate of the precision for the column chromatography separations for Fractions I and II.

Fraction II also contains squalene from the cod liver lipids. Values for squalene are not presented here because the lability of this compound renders it difficult to analyze quantitatively under the conditions we have employed for these analyses.

We have found that some lipid material precipitates out of hexane solution upon storage at 0°C. We were concerned that we would encounter problems in regaining a homogeneous mixture upon warming to room temperature. In the process of subsampling IDOE-5 for our own use and for the use of other laboratories we have cycled the extract from 0°C to 25°C to 0°C a number of times. Each time we have found that vigorous shaking after equilibration at 25°C is sufficient to obtain a sample which is homogeneous to inspection. Furthermore, the recent results reported in this paper demonstrate that chemical homogeneity has been maintained, at least with respect to hydrocarbons.

These results clearly demonstrate that it is feasible to prepare and store lipid extracts of this type for at least sixteen months. This is also of interest from the point of view of baseline studies and monitoring of areas where petroleum pollution may occur, e.g. offshore drilling or refinery locations. Economic feasibility may dictate that all samples obtained cannot be analyzed for hydrocarbons to detect petroleum pollution. However, it may prove feasible at least to extract the samples and store the lipid extracts. A few key samples from selected sampling stations could then be analyzed for hydrocarbons to determine whether petroleum pollution is present. If the key samples analyzed for a given time period indicate the onset of petroleum pollution or pollution on the increase, then all the samples from that given set could be analyzed to determine the extent and severity of the pollution. The results reported here indicate that it would be feasible to store lipid extracts for later hydrocarbon analysis.

Another facet of this work deserves mention. These analyses were performed satisfactorily by a college freshman under the direction of the authors. This demonstrates that the wet chemical and instrumental analyses required can be accomplished by a trained laboratory assistant supervised by professional scientists. We ask that all laboratories which have requested and received IDOE-5 subsamples report their results so that we may have a larger data base for statistical calculations.

We recognize that other methods and techniques have been, and will be employed in analysis of marine samples for petroleum pollution. Some are more sophisticated than the methods described here. However, more detailed intercalibration of all methods used in petroleum pollution studies is needed if we are to compare results obtained in different laboratories using various methods of analysis.

Acknowledgements:

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We wish to express particular thanks to E. Arthur Robinson, Jr., who performed the analyses reported in this paper and Drs. Werner Deuser and Oliver Zafiriou for their comments.

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Key Words: Gas chromatography, hydrocarbons, intercalibration, marine organisms, petroleum pollution.

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USE OF LOW MOLECULAR-WEIGHT-HYDROCARBON CONCENTRATIONS AS INDICATORS OF MARINE POLLUTION

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Dissolved low-molecular-weight hydrocarbon concentrations in surface water have been determined for several thousand miles of cruise tracks of the Texas A&M University ships, R/V Alaminos and R/V Gyre, in the Gulf of Mexico for the period from 1971 to the present. The hydrocarbon sniffer system and some of the results are reported in papers by Brooks [1,2] and Sackett [3]. The data generally indicate that the most important sources of C_1 through C_5 hydrocarbons are related to man's activities. These sources include ports and estuaries with their associated shipping and petrochemical activities, offshore drilling and production platforms, and ships which discharge oily ballast water and/or clean their fuel tanks at sea. The water column several miles distant from at least one example of each of the three types of sources showed several orders of magnitude higher concentrations than observed for the open Gulf. Natural seeps are also significant sources of hydrocarbons in the Gulf but the magnitude of their contribution relative to man's is probably very small.

On a recent cruise in March of 1974, we surveyed the water in and around several groups of platforms offshore Louisiana. The groups farthest out, presumably the newest, showed C_1-C_5 dissolved hydrocarbon concentrations in nearby waters generally two to three orders of magnitude higher than concentrations in surface water of the open Gulf of Mexico, where the latter are equilibrium concentrations determined by the partial pressures of the various gases in the atmosphere. Surface water around platforms nearer to the coast, presumably in place for a longer period of time than the platforms cited above, had much lower levels but still one to two orders of magnitude higher than open Gulf surface water.

Figure 1 shows the distribution of relative ethane concentrations (where the total open ocean surface values of C_2 hydrocarbons are set equal to one) around a group of platforms at 28°58'N, 92°00'W. All saturated C_2 to C_5 hydrocarbons, which are certainly petrogenic, as well as methane which may also be formed biochemically show approximately the same relative concentrations. The highest values, 85,000 times open ocean values or about 0.3 ml of ethane per liter of sea water, were found near what appeared to be an underwater "flare." This phenomenon, a large volume of gas bubbling to the surface at one spot, next to one platform, covered an area of about 100 square feet. High hydrocarbon levels, apparently from this one source, were observed in the surface water over an area greater than 25 square miles.

A very recent paper by Swinnerton [4] reports that approximately 90% of the dissolved C_2 hydrocarbons found in surface open ocean water is actually ethylene of biogenic origin. As our "sniffer" mode of operation does not differentiate between ethane and ethylene, the relative values for ethane and propane previously reported by Brooks [1,2] and Sackett [3] and shown in Figure 1 are minimal and the actual values may be an order of magnitude higher in many instances.

Three years of surveying and thousands of analyses confirm the popular sentiment that offshore petroleum production and tanker operations are contaminating much of the Gulf of Mexico coastal waters with petroleum derived low-molecular-weight hydrocarbons. This seemingly contradicts the conclusions of Koons and Monaghan [5] who state:

> "It is important to note that the C_1-C_2 values do not increase significantly with close proximity to the platforms....Producing operations are not changing the hydrocarbon content of nearby water."

It should be pointed out that their study included only a few analyses in the vicinity of South Timbalier Block 54 Field at just one particular time. No doubt, each field has its own set of pipelining, flaring, waste discharging, and other operational characteristics which determine the amounts of low-molecular-weight hydrocarbons being introduced into the surrounding water column. The magnitude of these inputs in the vicinity of any given platform presumably is not constant but changes with age and depletion of the field, weather, nearby production activities, leaks and breaks, etc. so that a few samples at a few sites may not provide a true measure of the annual discharge by such operations.

On the basis of our experimental data on the effects of low-molecular-weight hydrocarbons on primary producers, the biological effects of even the extremely high concentration levels

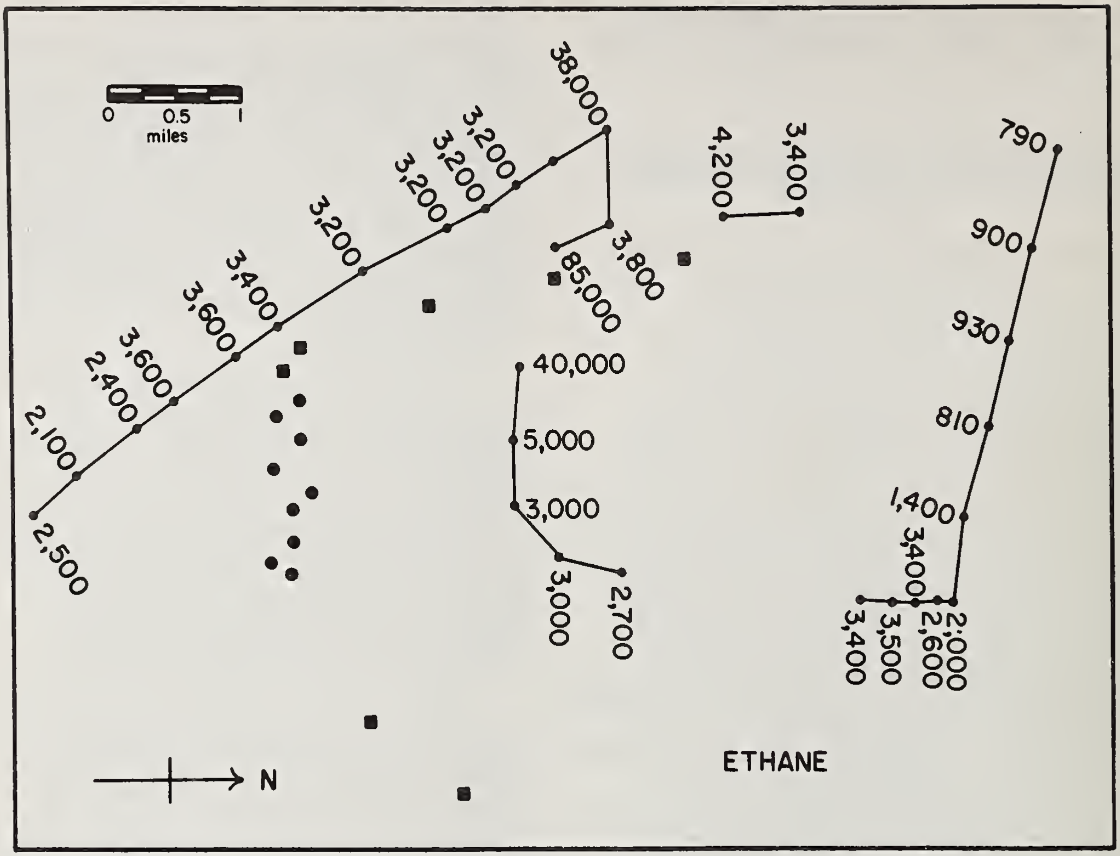

Figure 1. Relative ethane concentrations (1 = $3\text{x}10^{-6}$ ml of dissolved ethane at S.T.P. per liter of sea water) at 28°58'N, 92°00'W. Solid squares are locations of platforms; solid circles are exposed well heads.

observed around the group of platforms pictured in Figure 1 are probably negligible. However, in most instances, these comounds, which may be detected with great sensitivity, are indicators of the presence of the more difficult to measure, relatively soluble, highly toxic components of petroleum such as the aromatics and various nitrogen, sulfur and oxygen containing compounds. One exception to this generalization is an introduction from an operation producing dry natural gas containing very little C_3 and higher-molecular-weight constituents.

In summary, large areas of coastal water offshore Texas and Louisiana have up to six orders of magnitude higher concentrations of low-molecular-weight hydrocarbons than open ocean surface water. These high levels are most certainly petroleum-derived and due to offshore petroleum production operations. The observed high levels of C_1 to C_3 hydrocarbons do not seem to be detrimental to marine life, but nevertheless serve as sensitive indicators of the more toxic components of petroleum which usually are being simultaneously introduced to the ocean.

Acknowledgement:

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Key Words: Biological effects; Gulf of Mexico; hydrocarbon "sniffer"; low-molecular-weight hydrocarbons; marine pollution; pollution indicators; petroleum production platforms.

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FLUORESCENCE MONITORING STUDY AT OCEAN WEATHER STATION "P"

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In August and September of 1973 on Cruise 73-006 of the weathership, Quadra, a fluorescence monitoring study of seawater was carried out at Station "P" and along Line "P" (fig. 1) using a technique patterned after that of Levy [1] and Gordon [2]. Samples of seawater were obtained from the bow of the ship while it was proceeding at about 5 knots using a solvent washed 5 gallon stainless steel bucket and a nylon rope. A subsample of seawater of slightly more than 3 l was poured into a hydrocarbon free, one gallon glass bottle containing 60 mg of mercuric chloride. The bottle was sealed with a plastic cap having a teflon liner and stored in the ship's freezer. Another subsample of 1.5 l was extracted with two consecutive portions (65 ml and 25 ml) of methylene chloride. The combined extracts were placed on a hot water bath at 55° to 60°C and the solvent evaporated. The residue was taken up in 15 ml of cyclohexane and the fluorescent intensity at 383 nm was determined for an excitation wavelength of 308 nm. The fluorescent intensity was corrected for background contributions from the cyclohexane and the residual fluorescence of impurities in the methylene chloride and compared with standards of chrysene of similar concentrations.

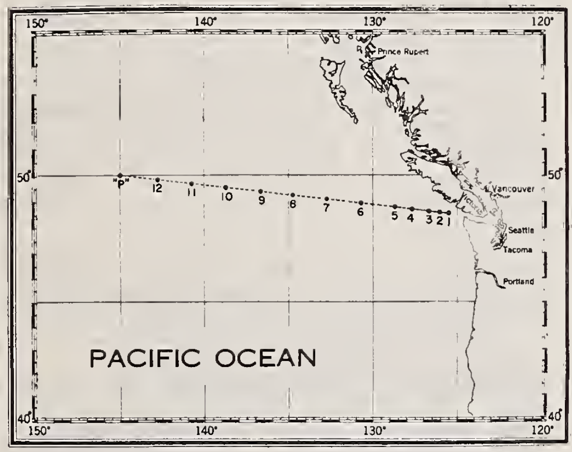

Figure 1. Chart showing Ocean Weather Station "P" and Line "P" positions.

Following the cruise of the Quadra, the preserved seawater samples were analyzed in the land-based laboratory in the same manner with the exception that a rotary evaporator was used to remove the solvent. The concentration of fluorescent compounds in chrysene equivalents as determined on shipboard and in the land-based laboratory are given in table I. The mean values for Station "P" seawater determined in the laboratory and on the ship were 0.031 ppb and 0.039 ppb, respectively with standard deviations of 0.018 and 0.020 ppb, respectively. The mean difference in paired values was 0.008 ± 0.007 ppb with a 90% confidence of the actual difference being within the range indicated [3]. By the same token, however, there is only about a 50% chance of there being an actual loss of 13%-28% (0.008 ± 0.003 ppb) in the original fluorescent intensity on storage for about two months. Although the results strongly suggest that there was a loss of fluorescent intensity on storage, there is insufficient precision and data to attach much significance to the mean difference between the shipboard and land-based laboratory results. Notwithstanding a loss of fluorescence on storage, the laboratory

Table I. Concentration in Chrysene Equivalents of Fluorescent Compounds on Line "P" and Station "P."

Station	Date (1973)	Lab.Anal.[a] Conc. (ppb)	Ship Anal.[b] Conc. (ppb)
2	Aug. 4	0.069	-----
5	Aug. 4	-----	0.017
6	Aug. 4	-----	0.035
7	Aug. 4	-----	0.038
12	Aug. 6	-----	0.019 0.024[c]
P	Aug. 8	0.071	0.08 0.11[c]
P	Aug. 11	0.035	0.48
P	Aug. 14	0.030	0.019
P	Aug. 17	0.028	0.031
P	Aug. 20	0.027	0.054
P	Aug. 23	0.060	0.040
P	Aug. 26	0.032	0.039
P	Aug. 29	0.018	0.027
P	Sept. 1	0.017	0.015
P	Sept. 4	0.013	0.031
P	Sept. 7	0.012	0.031
P	Sept. 12	0.025	0.034
P	Sept. 15	-----	0.045
12	Sept. 16	0.020	-----
10	Sept. 17	0.028	-----
9	Sept. 17	0.023	-----
7	Sept. 18	0.015	-----
4	Sept. 18	0.043	-----
3	Sept. 18	0.018	-----
2	Sept. 19	0.092	-----
1	Sept. 19	0.082	-----

[a] samples were preserved with mercuric chloride (ca, 60 mg/gal). [b] samples were worked up immediately without the addition of preservative. [c] duplicate determinations on same seawater sample.

results, which were obtained under scrupulously hydrocarbon-free conditions, confirm the low level of fluorescent compounds detected by shipboard analysis of seawater at Station "P" and along Line "P." The average value of 0.039 ppb, for Station "P" seawater, if converted from chrysene equivalents to equivalents of a typical Bunker C oil, would correspond to about 0.2 ppb. This value is about an order of magnitude smaller than the least amount which, it is claimed [2], might be confidently attributed to petroleum pollution.

Chrysene was chosen as an analytical standard for residual or weathered crude oils after consideration of over three dozen different compounds. Among considerations taken in this choice was the knowledge that the oils of interest in general exhibit a excitation maximum in the region 290 nm to 330 nm and an emission maximum in the region 360 nm to 400 nm as indicated by a number of samples studied in our laboratory as well as other laboratories [1, 2, 4, 5]. A further consideration was that a suitable standard should be obtainable at low cost and in high purity, particularly with regard to fluorescent impurities. As shown in figure 2, chrysene exhibits maxima in the desired range in both its emission and excitation spectra. Chrysene can be obtained in better than 99% claimed purity for about 10 cents a gram. Further, our sample of chrysene chromatographed on silica gel as a single compound for the purpose required as shown by fluorescence, ultraviolet and refractive index monitoring of the column effluent. The chromatographic behavior supported the claimed purity in the case of chrysene, but did not in the case of some other compounds which otherwise were good candidates for the standard.

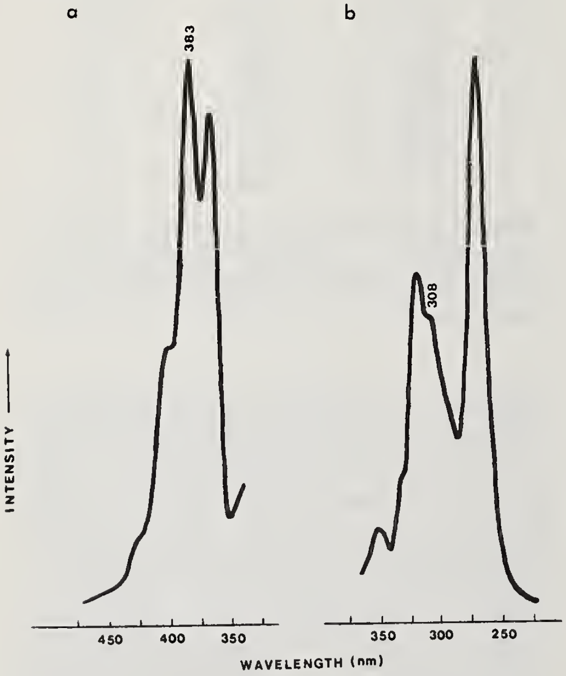

Figure 2. a. Emission spectrum of chrysene with exciter at 308 nm. b. Excitation spectrum of chrysene with analyzer at 383 nm.

Although there are certainly other suitable standards, we feel that chrysene best fits the criteria as seen by ourselves. At any rate we strongly favor the choice of a single compound, or perhaps a mixture of a few compounds, as a standard since such a choice would mean that the standard would be readily available to researchers through chemical supply houses obviating a large controlled supply as would be necessary in the case of an oil as standard.

Following the laboratory analysis of Station "P" and Line "P" seawater, the samples were stored at 5°C for an additional six months. By this time, following Zsolnay's lead [6,7], a combined High Speed Liquid Chromatography-Fluoreescene Spectroscopy (HSLC-FS) method was being used routinely for the analysis of seawater. A Waters Associates model 202/401 liquid chromatograph was interfaced with a Perkin-Elmer model 204 fluorescence spectrophotometer by means of a flow-through cell (0.1 ml internal volume). A 150 mm x 1.8 mm column packed by the balanced density method [8] with 5 μ silica gel (LiChrosorb Si-60, E. Merck Co) was used with a flow of hexane at a rate of 0.5 ml/min. The exciter and analyzer settings on the fluorescence spectrophotometer were 308 nm and 383 nm, respectively. Under these conditions the center of the chrysene band passed into the fluorometer cell in about 6.5 min as shown in figure 3c. The seawater samples from Line "P" and Station "P", some of which had been combined prior to storage to give sufficient quantities for analysis, were extracted as before. The extract, however, was ultimately taken up in 0.5 ml of hexane instead of 15 ml of cyclohexane and a 0.05 ml portion injected on the column. The results of two such injections for different samples are shown in figures 3a and 3b and can be compared with the result of an on column injection of 830 pg (in 0.05 ml of hexane) of chrysene at the same instrument sensitivity.

A second extraction was performed on each sample of seawater to check on the efficiency of the first extraction and as an additional check on the solvent purity and cleanliness of equipment. If any fluorescent compounds were extracted in the second extraction, their contribution was added to the contribution of the first extraction. Blanks were run on each new batch of solvent or whenever there was an indication of contamination and a blank correction applied to each sample run. The area under each curve was determined with the aid of a Disc integrator and converted into equivalents of chrysene. Chrysene standards were run periodically as a check on the sensitivity of the instrument.

The result of the HSLC-FS analysis are given in table II. The average value in chrysene equivalents for the Station "P" samples was 0.016 ppb with a standard deviation

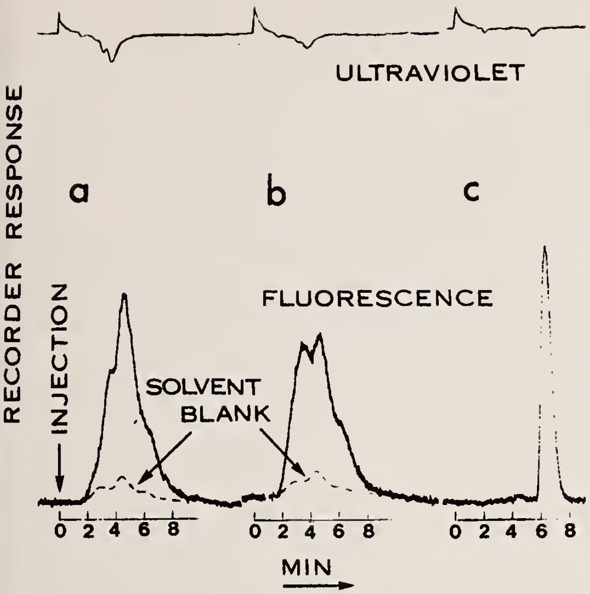

Figure 3. a. chromatogram of the extract of the seawater sample of Sept. 7. b. chromatogram of the extract of the combined seawater samples of Aug. 14 and Aug. 17. c. chromatogram of 0.83 ng of chrysene.

Table II. Concentration in Chrysene Equivalents of Fluorescent Compounds on Line "P" and Station "P" as determined by Combined High Speed Liquid Chromatography-Fluorescence Spectroscopy.

Cruise	Station	Date (1973)	Concentration (ppb)
73-006	2	Aug. 4	0.026[a]
73-006	P	Aug. 14,17[b]	0.019
73-006	P	Aug. 20 Sept. 12[b]	0.014
73-006	P	Aug. 29, Sept. 1,4[b]	0.018
73-006	P	Sept. 7	0.011
73-006	9	Sept. 17	0.027 0.025[c]
73-006	4	Sept. 18	0.012 0.010[c]
73-009	P	Dec. 14	0.013
73-009	P	Dec. 30	0.018

of 0.0033 ppb. The standard deviation was considerably smaller than in the previous determinations. This result may be a reflection of increased operator experience in extracting the seawater samples or of an inherently better precision in the method. The average value is close to one-half that determined for the Station "P" samples in the previous laboratory analysis. This is also true if the subset of samples which were analyzed on both occasions is considered. The further reduction of fluorescent intensity of the seawater extractables indicates either a further loss of fluorescent compounds on extended storage or the impeding of the passage of polar fractions of fluorescent compounds through the silica gel column. That the latter possibility may be true, to some extent, is indicated by the appearance of very broad fluorescent bands from the column after heavy use for a few weeks. Acetonitrile, methylene chloride and carbon tetrachloride provide a convenient elution series for cleaning the column.

This initial fluorescent monitoring study, we feel, provides a reliable indication of the level of fluorescent compounds in oceanic water off the Canadian West Coast against which any increases attributable to future vessel traffic on the coast can hopefully be measured. Additional studies to supplement those in this report are anticipated to provide a more extensive baseline and determine, if possible, the origin of the compounds measured. We believe that the HSLC-FS method is more useful than the original fluorescence method since it has the capability of providing more information with the same input of work. In the study herein described, nevertheless, the two methods definitely gave comparable results and an exacting intercalibration of the methods is certainly warranted.

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Key words: Fluorescent monitoring, Pacific North East; chrysene standard; combined High Speed Liquid Chromatography-Fluorescence Spectroscopy.

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[a] A liter sample was extracted. [b] The samples taken on these dates were combined to provide enough seawater for analysis. [c] Duplicate determination on same seawater sample.

TOPICAL SESSION IV.

Oil in Marine Organisms and Sediments: Sampling and Analytical Methods

NBS Spec. Publ. 409, Marine Pollution Monitoring (Petroleum), Proceedings of a Symposium and Workshop held at NBS, Gaithersburg, Maryland, May 13-17, 1974 (Issued December 1974).

SAMPLING MARINE ORGANISMS AND SEDIMENTS FOR HIGH PRECISION GAS CHROMATOGRAPHIC ANALYSIS OF AROMATIC HYDROCARBONS

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Sampling techniques for the collection of sediment samples and inner tidal organisms have been developed as part of a hydrocarbon baseline study in Prince William Sound Alaska. All of the samples were collected during low tides and therefore only hand collection methods have been considered. The sample collection experiments were designed to reflect seasonal, species, and geographic variations during a one year period and to be complimentary to a continuing biological baseline study in the same area.

Sample collection for baseline studies in the sub-part per billion to part per million concentration range from pristine environments, such as Prince William Sound, requires that every possible precaution be taken to minimize contamination and sample handling errors. At these ultra-low concentrations, it is imperative that a creditable sampling program be designed in order to obtain meaningful results and because the high cost per sample limits the number of samples which can be analyzed. At the same time, samples must be statistically representative, collected in a reproducible manner, and taken in such a manner as to not perturb the species population and distribution.

New wide mouth glass jars were cleaned in the laboratory prior to use by the following sequence:

(1) Soap and water wash,
(2) Multiple distilled water rinses,
(3) Acid wash in concentrated H_2SO_4 for $\geq$ 5 min.,
(4) Eight (8) rinses in distilled water,
(5) Two (2) rinses with hydrocarbon-free water,
(6) Rinse with singly distilled methanol (from reagent grade),
(7) Two rinses with doubly distilled n-pentane (from reagent grade), and
(8) Flushed with N_2 vapor taken directly from a LN_2 source.

The organic free water was prepared by redistilling distilled water over $KMnO_4$-KOH and pumping through a 90 cm by 2.5 cm preparative scale liquid chromatography column. The column was packed with XAD-2 resin which was previously cleaned by Soxhlet extraction with acetonitrile for 24 hours and methanol for 48 hours. The purpose of the N_2 flushing before sealing was to provide a bacteria-free, inert atmosphere. Aluminum bottle cap liners were used to make an air-tight seal in the bottles. The liners were cleaned in a sonic cleaner with acetone and pentane, successively.

Polyethylene gloves were used by all personnel in order to avoid contamination by body oils. Although rubberized rain gear was generally required, all samples were collected with all personnel, boats, and other craft located such that the tidal wash was away from the sample. Access to the sample sites was by float-plane, cruiser, or ship. In all cases these craft and shuttle skiffs to shore were well removed from the sample site. This minimized contamination of the samples from residual oils and hydrocarbons from the boats. In addition, wading boots were cleaned by wading long distances in the mud and water.

Sediment samples were collected from mudflats, glacial or other fresh water outflows, rocky inner-tidal flats, sandy inner-tidal flats, and from a remote control site. Sampling was effected by taking two vertical cuts for each sample with a Plexiglas right circular cylinder 5 cm. i.d. by 8.8 cm. long and trimming the excess sediment with a clean stainless steel spatula. No attempt was made to drain the water, or remove debris, rocks and small biological specimens. Samples were not collected under areas covered by moss. Each sample was sealed and immediately stored in an ice chest over dry ice and thereby quick frozen.

Sediment sampling was done in two different modes to characterize different sampling sites. Some areas were characterized by sampling in a small localized area to help insure uniformity of samples. Others were sampled by taking a cross-section at regular intervals between the low-low tide and the line at high tide. The latter method was used where very large areas were exposed by changes in tidal levels. The cross-sectional sampling method appears to show a larger sample variability but was thought to be more representative of the sampling site. These samples show marked differences in their hydrocarbon profiles because of the differences in biological content in the samples, the presence of decaying vegetation, animal wastes, etc., and because the extent of water coverage varies markedly, depending upon where the sample is collected.

No attempt was made in the laboratory to blend all of the samples taken from a given site because homogenization of grossly heterogeneous samples is not feasible. Therefore, each site was characterized by five discrete samples. Large rocks were not used as part of the laboratory sample, but otherwise the sample was defined as the sample collected in the field.

The inner-tidal organisms listed in Table I were chosed as being representative of the area, because of their differences in feeding and migratory habits, and reproduction rates, and to coincide with species for which biological baseline data was being collected.

Table I. Biological Samples Collected

Sample	Biological Significance	Form for Analysis
Macoma (small clam)	Deposit Feeder	Frozen, in shell.
Mytilus (mussel)	Suspension Feeder	Bissel threads removed. Organism quantitatively removed from shell.
Acmaea (limpet	Grazing Feeder	Quantitatively removed from shell while frozen.
Cancer Magister (dungeness crab)	Bottom Feeder	Tissue, gills and organs removed and homogenized.

Macomas were collected by shoveling surface sediment into shaker screens (with 1/4 inch wire mesh) in order to wash out sediment, silt, and small debris in the tidal water. Large sampling areas ($>$1000 ft^2) were needed to collect quintuplicate samples of 100 g each. All work was done with pentane rinsed stainless steel spatulas and polyethylene gloves. The final sorting of debris and Macomas was done by hand before quick freezing the samples over dry ice.

Adult Mytilus and Acmaea were collected directly into the glass jars by prying them loose with spatulas. Crabs were collected from crab pots and quick frozen in polyethylene bags. In all cases, 100 grams was required for each sample of each specimen, and quintuplicates were collected in all cases.

Both sexually mature and immature Fucus (macro algae) were collected from different tidal levels at each sampling site in 64 oz. jars by cutting samples at the base of the stem. However, it is very difficult to select a representative amount of mature Fucus and this error will be reflected as a sampling bias and give a larger apparent biological variability. Only Fucus attached to a rock or sediment base was used in order to avoid drifting samples and to insure that the sample was taken from a stable colony. It was felt that a true cross-sectional sample of the Fucus should be taken to represent changes in tidal levels and to reflect differences in exposure to the air, sun, and water.

Finally, an attitude and approach to field sampling has evolved which appears to be successful. First the design of the sampling program and the choice of methods to be used should be implemented in terms of the methods of analysis to be employed. Personnel in charge of collecting samples should be thoroughly familiar with the precautions to be taken during sample collection and handling, and be cognizant of the many possible sources of contamination. It has been our experience that it is highly desirable that the chemists responsible for the laboratory analysis participate with biologists in the field sampling and that good rapport and cooperative working relationships between field and laboratory personnel be maintained. In this manner, the laboratory data can be most effectively analyzed in terms of the limitations and considerations of field sampling. Conversely, field sampling experiments can be more effectively designed once the errors and procedures of the laboratory analysis are thoroughly understood.

Key Words: sediment, biological tissue, baseline studies, sampling, hydrocarbons, contamination.

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FIELD SAMPLING METHODS AND TECHNIQUES FOR MARINE ORGANISMS AND SEDIMENTS

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Grice et al [1] reported on the solution of problems associated with collection and preservation of open ocean marine organisms for pollutant analysis. Field sampling programs in inshore and intertidal areas in Southern California encountered many of the same problems which required similar solutions. This paper addresses itself to the difficulty in obtaining representative data to describe levels of petroleum content of sediments and organisms in an area.

Most of these field sampling problems are the result of the uneven petroleum distribution in the marine environment. This applies to the water column, sediments, organisms and tissues. It is only in exceptionally large oil spills, near the source of a spill, or in enclosed areas, that large areas are coated with oil. In the open ocean, soluble components usually do not reach the ocean floor except in shallows with high wave action. However, the circumstance is different in enclosed areas where the oil may become trapped or if the oil is released through cracks in the ocean floor. As oil which leaks from submarine faults rises to the surface, some soluble components enter the water column.

In areas such as Coal Oil Point, natural petroleum compounds enter the ocean in several different ways:

- gas bubbles which move rapidly to the surface
- oil which moves rapidly to the water surface. (This could be almost a continuous flow such as that observed by divers in June 1973, which emanated from holes described as the size of gopher holes (~7.5 cm. diameter)
- bubbles of oil which gradually appear on the surface of the substrate and then move to the water surface
- oil which appears on the sediment surface as a sticky tar which may gradually float free to the surface, drift with negative buoyancy, or simply spread through bottom sediments.

Location of such emission sites is frequently difficult because of their intermittent nature. Hence, a benthic sampling program could not necessarily be designed around the detection of active emission sites at a particular time.

Much of the seep oil and tar from the Coal Oil Point area may be deposited in the trough of the Santa Barbara basin (Fischer and Berry [2]). Kolpack [3] determined that the Santa Barbara basin contains spill oil, and Oguri [4] reported that material in trawls taken in the Santa Barbara basin was oily.

Therefore, in areas such as the Santa Barbara Channel, sediments and organisms will not be evenly exposed to petroleum compounds. This complicates sampling problems to determine:

1) where to obtain representative samples of the area,

2) what sample sizes are needed,

3) how many samples are needed, and

4) when and how frequently samples should be taken.

A further problem may be created by periodic exposure to oil. Ampaya and Mikolaj [5] reported periodic changes in oil seepage rate based on data from a seep near Coal Oil Point, whereas the present author has noted variations in the amount of tar on sandy beaches adjacent to the Santa Barbara Channel. More tar was present on beaches towards the Southern end of the Santa Barbara Channel in the period March through May than at other times of the year (unpublished data gathered 1971-74). This may not be a reflection of wind and current direction. Areas may also be seasonally or intermittently exposed to oil pollution from man's activities.

A. Location of samples representative of an area will depend on the size and geologic setting of the area. For example, open coastline areas where there are no adjacent sources of oil can doubtless be characterized by samples at different depths of both sediments and organisms. However, sampling of an area of intermittent oil seepage poses a different problem. The amount of oil in the sediments will vary both horizontally and vertically. The vertical variation on a beach will be due in part to a combination of different rates of oil deposition and in part to sedimentary movements.

Table I. Total CCl_4 Extractable Organics (mg/l) in Sediments Related to Depth in Water and Sediments.

Water (m) Sediment (cm.)	20	40	60
* 0 - 5	565	4,500	4,200
5 - 15	4,800	8,100	8,000
* 0 - 5	285	22,500	4,350
5 - 15	4,500	25,000	6,200
0 - 5	1,300	5,200	6,600
5 - 15	4,500	9,200	
0 - 5	570	17,000	9,800
5 - 15	6,100	60,000	

* Average of duplicate samples.

Table I illustrates the difference in total CCl_4 extractable organic content in box cores of sediments from a natural oil seep area in the Santa Barbara Channel, as determined by infrared analysis. In all cases, the total organic content is higher 5-15 cm. deep in the sediments than in the top 5 cm. of the sediments. The total organic content is also lower in the shallow water (20 m.) samples than in the deeper water (40-60m.) samples. In all these samples, grain size is approximately equivalent. These trends are generally consistent with other available data, but the trend of increasing total organic content with depth is interrupted by the presence of natural petroleum seeps.

The surface area of a box core was 21 x 29 cms. Duplicate samples were collected in the top 5 cms to determine the variability over the surface area (Table II).

Table II. Total CCl_4 Extractable Organics (mg/l) in Duplicate Sediment Samples Collected in the top 5 cm. of the Box Core Samples.

Sample			% Difference
1	110	460	318
2	340	390	15
3	400	730	82
4	3,800	4,600	21
5	4,000	4,700	18
6	4,200	4,800	14
7	5,200	5,800	12
8	20,000	25,000	25

% Difference was calculated on the lowest value.

The variation in this set of 8 duplicate samples collected in an area of natural oil seepage demonstrates the danger of using isolated samples as a baseline figure without some idea of the variability in the area. Juge [6] also reported the variability of petroleum content of sediments within a single box core.

Hence an area such as the Santa Barbara Channel would require:

- a sampling program related to water depth in non-oil seep areas to account for the variation in accumulation of petroleum with water depth
- a sampling program within one or more of the oil seep areas to determine the level of petroleum accumulation adjacent to oil seepage
- sampling of sediments from different depths to determine if there are variations in petroleum deposition, sand movement, or surface oxidation.

Sediment grain size must be considered in all cases.

B. Sample size should be determined empirically. The lower limit is determined by the minimal amount of material necessary for adequate chemical analysis. Warner [7] determined that, for hydrocarbon analysis of sediments in Southern California mainland shelf areas, a sample of approximately 120 ml. is required. Naturally, less material would be required for sediments with a high hydrocarbon content than for those with low hydrocarbon content. However, as the hydrocarbon content is generally unknown at the time of collection, this minimal sample size should be collected.

It is impossible to make a general rule on optimum sample size. A constant sample size will result in over-sampling and an increase in preservation and storage problems.

Optimal sample size can be determined for each area and/or type of situation. A subjective assessment of sample size can be determined by analyzing multiple samples of known volume. The mean is then calculated on a cumulative basis and plotted against sample volume. The optimum sample size occurs where variation ceases and the curve flattens (Fig. 1). Naturally, the larger the sample size, the more accurate the information; but as the curve flattens, the increase in information decreases and becomes less important (based on Kershaw [8]). The optimal sample size is (5x120 ml. = 600 ml.). If these 5 samples are analyzed separately rather than as a composite, then an indication of the variability in content within a small area will be obtained.

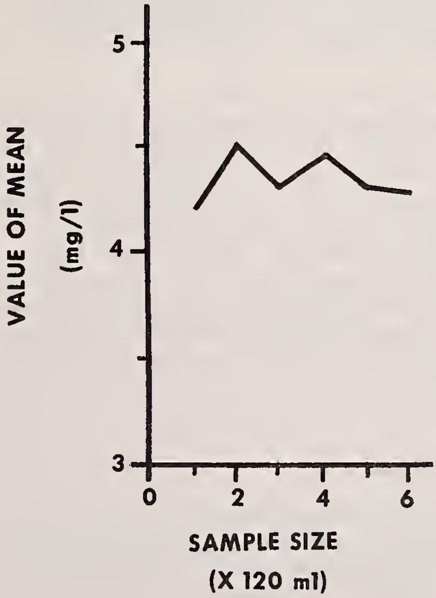

Figure 1. The reduction of the variations in the value of the mean, as the size of the sample is increased.

C. <u>The number of samples</u> required to characterize an area can be determined using the same rationale as that used to determine sample size.

D. <u>Timing and/or frequency of sampling</u> are less important in the open ocean, where seasonal effects and man's activities are least variable. However, changes in ocean currents could result in seasonal changes in exposure of sediments and organisms to petroleum hydrocarbons. In nearshore areas, where seasonal trends are greater and where pollution will have a greater effect on the environment, sampling should be seasonal.

Sampling of tissues

The same procedure should be used to determine the distribution, size, number, and frequency (timing) of sampling animals. The minimal sample size of tissues used in the field sampling program in Southern California was 10 gm. While this was more than adequate for tissues containing high levels of petroleum hydrocarbons, it was only adequate to hydrocarbon levels as low as 2 ppm.

Containers and Preservation Methods

All sediment and tissue samples were frozen. Samples were retained in a normal freezer (-20°C) or on dry ice during field trips and transportation, but long term storage was in a freezer maintained between -70° and -80°C. This low temperature was used to eliminate changes due to biological processes which can occur at "household" freezer storage temperatures [9].

This method of preservation imposed some limitations on the type of storage containers used. For example, some glassware could not withstand these low temperatures. Other sampling containers found to be unsuitable included aluminum foil and paper -- the former because foil is often coated with oils or grease during manufacture and the latter because it tends to stick to tissues during freezing and thus contaminates the samples. Plastics other than Teflon were generally not suitable for storage or collection.

Clean aluminum cans and glassware were used for sediments and tissues respectively. Cans and glassware can be adequately cleaned prior to use.

Contamination of samples results from:

1. contaminated collection equipment,
2. preparation of samples for preservation,
3. passage of sampling equipment through surface slicks,
4. boat exhausts.

These problems were detailed by Grice et al. [1].

In intertidal areas, hand tools can be cleaned between collection of samples. Visible compounds can be scrubbed from the surface of such equipment using detergents, and then rinsed well in clean water and acetone and finally dried.

Sampling to determine the presence of petroleum in animal tissues involves several unique problems. Foremost is the difficulty in insuring that the petroleum is in the tissues rather than passing through the gut at the time of collection. If the animal is large, it can be dissected and the gut contents removed. However, sampling benthic infauna provides a further challenge. The animals are generally very small and many of them feed by passing sediments through their gut. In a heavily contaminated area, only a few grains of sediment either on the animal or in the gut increases the error of hydrocarbon tissue analysis to an unacceptable level.

Assuming that all external sediments are removed, the problem of removing sediments from the gut is of paramount importance. Dissection of fresh animals of this size (possibly only a few mm. wide and/or long) is impossible on a ship and dissection after freezing is impossible because the freezing process damages tissues. Dissection also results in loss of body fluids. This is unacceptable in small animals with a high percent of body fluids.

A more practical method is maintance of small live organisms in clean seawater to allow them to eject gut contents prior to preservation. If this is done in a closed container, the animals may reingest their faeces. Hence, such a program should involve a running seawater system with some method of removing defecated material. This is not as simple as it appears, because egested material is frequently almost as large in diameter as the body of the animal (polychaete) from which it originated.

Just how significant contamination could be can be demonstrated by data from trial analyses of sediments containing 4,100 mg/g total CCl_4 extractable organics. A value for extractable organics as high as 1,000 μg/g was recorded in the detritus removed externally from the animals in one sample, while only 40μg/g extractable organics was recorded in the animals.

It is apparent that only a very small amount of sediment in the gut of these animals can render the value meaningless. While the actual percentage of contamination in the tissues is unknown, it is obvious that this particular infaunal sample had a very low level of contamination compared with the surrounding sediments.

Use of a continuous flow-through system such as used in depuration experiments, is suitable for larger animals such as mussels. However, such a system needs careful experimentation to determine the time required to remove only gut contents without depuration of petroleum compounds from the tissues. Depuration of some petroleum compounds can occur within a matter of hours (Anderson [10]).

An additional problem involves contaminated water trapped within molluscan shells. Here the problem is not as critical as in the case of sediments, because the concentration of petroleum in seawater is probably lower than that found in organisms. However, this water should be carefully removed prior to tissue analyses. After freezing, this can easily be accomplished by simply removing all the ice when the shell is opened for tissue analysis.

Acknowledgments

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METHODS FOR ESTABLISHING LEVELS OF PETROLEUM CONTAMINATION IN ORGANISMS AND SEDIMENT AS RELATED TO MARINE POLLUTION MONITORING

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Petroleum hydrocarbons in marine organisms and sediments have been extracted, separated, isolated, identified, and quantified by a number of methods. Since no single technique provides a complete analysis of petroleum residues in organisms, some consideration for selecting methods and for understanding potential problem areas are presented.

Petroleum is derived from the decomposition, at high temperatures and pressures, of plants and animals buried for millions of years. Hydrocarbons are not foreign to the marine environment; they are synthesized by most, if not all, living organisms. Several detailed reviews of the distinguishing characteristics between hydrocarbons native to marine organisms and sediment and those found in petroleum have been prepared [1], [2], [3].

In order to decide what combination of analytical procedures will be most useful, the analyst needs to determine the level of sensitivity and selectivity necessary to meet the requirements of his scientific goal. For example, if one wishes to demonstrate only high-level uptake ($> 10^{-6}$ g/g wet weight, yet below detectable odor and taste levels) of certain petroleum components in marine tissue, then less sensitive techniques need be used than if lower biogenic levels (10^{-9} g/g wet weight or less) are investigated.

Contamination

Fossil hydrocarbons are ubiquitous compounds which can cause serious problems and create artifacts for the unwary in the laboratory. Once the analyst has established his lower limit of sensitivity (or detectability), then contamination of solvents and chemicals must be investigated. True biogenic baseline levels of hydrocarbons are only obtainable by purifying solvents and chemicals. Table I lists some typical levels of n-paraffin hydrocarbon contamination routinely found in laboratory chemicals, solvents, and materials. To insure that contaminants do not exceed levels which would make the isolation of the same compounds from organisms meaningless, it is essential that the complete extraction and analytical procedure be carried out routinely without the sample. A rule of thumb might be that the solvent/chemical blank should contribute less than 10% of the total signal from an organism sample.

Extraction

Before the sample is extracted, the actual method of weight determination must be expressed on some standard weight/weight basis. If wet weight is chosen as a basis, then the moisture content of the sample should be provided. If the sample has been frozen, body fluids contained in the frozen aqueous portion from ice-ruptured membrane and cellular structures should not be lost during a draining step.

A number of methods have been presented (table II, based on the background material presented in references [2] and [4]) for removing the lipid fraction from biological and sediment samples containing hydrocarbons. Soxhlet extraction of minced, homogenized, or sonified tissue samples is routinely used for removing lipids with a recycling solvent system. Schmid, et al. [5] experimentally applied solubility parameter theory to the properties of solvent extraction from moist biological membranes and found that the successful separation of lipids from proteins in undenatured membranes required (1) solvation of the water in the organic phase of the extracting solvent system, and (2) optimal solubility for both the relatively nonpolar neutral lipids and for polar lipids. Their studies indicated that a binary solvent system using an aromatic hydrocarbon and a low molecular weight alcohol proved efficient.

Table I. Typical levels of background hydrocarbon contamination in laboratory chemicals, solvents, and materials (extracted with benzene, expressed as n-C_{14}-C_{37}).

Chemicals/Solvents		Found	After Purification
Glass-distilled, commercial			
Pentane		56.2 µg/l	<2.5 µg/l
Benzene		100 µg/l	<2.5 µg/l
Cold tap water (in pentane)		0.92 µg/l	-
Na_2SO_4	Brand A	30-35 ng/g	12-18 ng/g
	Brand B	17 ng/g	
	Brand C	108 ng/g	
	Brand D	245 ng/g	
$MgSO_4$, anhydrous		12.1-130 ng/g	4.8 ng/g
Sand, Ottawa		10.1-369 ng/g	4.9 ng/g
NAOH, dissol. tap water		<5 ng/g	-
Materials			
Aluminum foil	Brand A	7.1 ng/cm^2	
	Brand B	8.6 ng/cm^2	
Asbestos cord		<5 ng/g	
Glass fibre (wool)	1st extr.	18.3 ng/g	
	2nd extr.	1.96 ng/g	
Glass microbeads	1st extr.	50.9 ng/g	
	2nd extr.	6.69 ng/g	
Laboratory wiping tissue		197 ng/cm^2	
Rinsings from fingers		100 µg/finger	
Rinsings from rubber gloves		230 µg/finger	
Soxhlet thimble, Nichrome wire		1,589 ng/thimble	
Ceramic,	1st extr.	1,309 ng/thimble	
	2nd extr.	444 ng/thimble	
Teflon®	3rd extr.	346,400 ng/thimble	
	4th extr.	40,660 ng/thimble	
	5th extr.	2,042 ng/thimble	

Table II. Extraction techniques of petroleum components from biological and sediment materials.

Extraction Technique	Application	Sample Requirements	Equipment Requirements
1. Soxhlet apparatus with MeOH, benzene, combination or other solvents of similar polarity.	Frozen samples Lyophilized samples Wet or fresh samples	As little as 1 g. wet or fresh; routinely 10-40 g. wet	Soxhlet apparatus; separatory funnels; rotary evaporator for concentrating extract.
2. Sonification, solvent extraction with CCl_4 and solvent above.	"	"	Sonicator probe or sonicator bath; separatory funnels, rotary evaporator.
3. Steam distillation coupled with solvent extraction, ethyl ether.	Frozen samples Wet or fresh samples	1-10 g. wet or fresh weight	Extraction flasks; steam distillation apparatus.
4. Homogenation, anhydrous Na_2SO_4 to promote cell disruption and remove water; solvent extraction: pentane or hexane.	Frozen samples Lyophilized samples Wet or fresh samples	As little as 1 g. wet or fresh; routinely 10-40 g. wet	Blender or homogenizer; tissue grinders or similar equipment.
5. Homogenation, anhydrous $MgSO_4$ and sand; hexane.	"	"	Mortar and pestle.
6. Digestion in alcoholic KOH.	"	"	Apparatus for refluxing.
7. Solvent extraction followed by saponification.	Lipid extract	10^{-3} g.	Screw can centrifuge tube with Teflon ® liner; centrifuge.
8. Helium stripping at 120°; water and hydrocarbon traps, gas chromatography.	Sediments, wet	0.5 g. Detect 1 ppm	Gas systems, efficient trapping materials; gas chromatograph.
9. Nitrogen stripping at 20°, stirred aqueous solution; GLC/MS.	Sediments, wet		Same as above; mass spectrometry.
10. Heat sample and vaporize directly into inlet system of MS.	Sediment, dry	0.05 g. Detect 1 ppm	Mass spectrometry.

Source: Based on background material presented in references [2], [4].

For certain fat-rich samples, Soxhlet extraction may not be as efficient or as rapid as an alkaline digestion. An alkaline digestion, or saponification of a previously concentrated lipid extract, also permits the removal of fatty acid esters which may interfere with subsequent chromatographic separations. On the other hand, if an analyst needs to extract a wide range of samples (fresh, frozen, soft- and hard-bodied organisms, algae, sediments and aged petroleum residues) by a single procedure, then a Soxhlet extraction provides a suitable method for almost all types of environmental samples. Homogenization of wet, soft tissue in the presence of Na_2SO_4 or $MgSO_4$ is a rapid method, but extraction efficiency with the commonly-used nonpolar solvents may not be as great as with mixed solvent systems.

Low molecular weight hydrocarbons from sediments can be obtained semiquantatively with gas stripping combined with collection in micro gas chromatography columns or cold traps. This trapped material can then be flashed into a gas chromatograph or into a mass spectrometer; the entire sample is consumed in a single analytical determination. It is important to remove elemental sulfur from sediment extracts prior to hydrocarbon analysis to avoid interference.

Chromatography

The characteristics of the separation of the lipids into hydrocarbon classes depend upon the choice of chromatographic techniques (table III). Thin-layer chromatography (TLC) and paper chromatography provide simple and rapid separations of hydrocarbon classes from non-hydrocarbons, and a TLC plate can be used with ultraviolet or fluorescence spectrophotometry or with H_2SO_4 charring to produce quantitative estimate of specific hydrocarbon classes or groups of compounds. However, for biogenic baseline levels these methods usually lack the precision, specifity, sensitivity, and accommodation to sample size loading available with column chromatography. High pressure liquid and gel permeation chromatography are useful techniques which may gain wider acceptance in the future.

If one decides to use liquid-solid (column) chromatography, it is necessary to choose the proper adsorbent or combination of adsorbents with the most advantageous activity and mesh size for the length and diameter of the column. Additional decisions must be made as to loading (adsorbent/sample: v/w), solvent systems and fraction volumes. Column chromatography commonly uses silica gel for separating hydrocarbons from

Table III. Chromatographic separations of petroleum components from biological and sediment materials.

Separation Technique	Components Separated	Application	Sample Requirement	Equipment Requirements
1. Column chromatography	Hydrocarbon-type analysis to alkanes, alkenes, aromatics, and from N, S, O heterocyclics	Biological and sediment material extracts	10^{-4} g.	Standard column chromatography
2. Thin-layer chromatography	Hydrocarbon-type analysis	"	10^{-5} g.	Standard TLC chromatography equipment; UV and densitometer
3. Paper chromatography	"	"		Standard paper chromatography equipment
4. High-pressure liquid chromatography	Ring number separation of aromatics; separation by hydrocarbon types	"	10^{-4}-10^{-2}	High-pressure liquid chromatograph
5. Gel permeation chromatography	Molecular weight separation	Primarily for heavier molecular weight components	10^{-4}-10^{-2}	GPC equipment

Source: Based on background material presented in references [2], [4].

non-hydrocarbons or alumina for separating high molecular weight polar compounds; a dual column of alumina packed above silica gel successfully takes advantage of both adsorbents. Deactivation of the adsorbents with water (to 5%) prevents formation of hydrocarbon artifacts from biogenic hydrocarbons. Nonpolar solvents (usually pentane or hexane depending on degree of volatility desired) can be used to elute the saturated hydrocarbons from the column, and the application of more polar solvents (benzene, CCl_4, CH3OH, acetone) allows the removal of the more polar hydrocarbon and non-hydrocarbon compounds. The efficiency of the packed column must be determined occasionally with standard compounds.

Identification and Quantification

Again, a variety of techniques have been tried (table IV) for identifying and quantifying petroleum residues in biological samples and sediments. Gravimetric methods for quantitatively determining petroleum pollution are useful only with relatively high concentrations (10^{-4} g) of a total fraction weight. Spectrophotometric methods usually provide rapid estimates of the total absorbance or fluorescence of all materials at a specific wavelength, but they give little indication of the complexity or molecular weight range of a sample. These approaches provide limited discrimination between biogenic hydrocarbons and those contributed from petroleum pollution. If a known pollutant with a reproducible absorbance or fluorescence characteristic is present (from an oil spill or bioassay experiment), then spectrophotometric methods are often used as quick, simple and sensitive monitoring tools.

Gas chromatography provides both a separation and a quantitative estimate of specific compounds based on their boiling points and polarity with

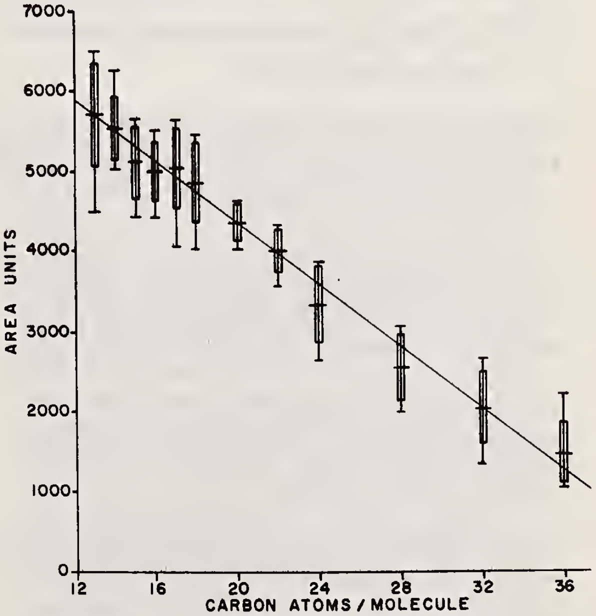

Figure 1. Typical gas chromatograph calibration curve using parameters given in table V, based on nine (9) determinations over a 7-day period. Symbols represent the range, mean and standard deviation; average percent std. dev. (100% x std. dev./mean at each carbon number) was 11.4%; curve fit by eye. Individual hydrocarbon concentrations were 1.015-1.396 µg/injection.

Table IV. Quantitative techniques for the identification of petroleum components in biological and sediment materials.

Identification Technique	Components Determined	Extract Sample Size	Equipment Required
1. Gravimetric	Non-volatile extractables	10^{-4}-10^{-2} g.	Glassware, analytical balance
		10^{-6} g.	Micro balance
2. UV absorption spectrophotometry	Conjungated polyolefins; aromatics	10^{-3} g.	UV absorption spectrophotometer;
3. Infrared spectrophotometry	C-H and C=O; C-H stretch-freq. (2,930 cm^{-1})	10^{-3} g.	Low resolution infrared spectrophotometer
	Total hydrocarbon		High resolution IR spectrophotometer with scale expansion
4. Fluorescence spectrophotometry	Unsaturated compounds; aromatics	10^{-6} g.	Fluorescence spectrophotometer
5. Gas chromatography	Individual hydrocarbons		Gas chromatograph
Low resolution	Hydrocarbon profiles and boiling range of sample	10^{-3} g.	
High resolution	More detailed hydrocarbon profiles; sulfur profiles; n-paraffin/isoprenoid ratios; depends on column and on detector.	10^{-9} g.	
6. Mass spectrometry	Hydrocarbon types and molecular identification	10^{-6} g.	Low resolution MS of 60-600 mass range
7. Gas chromatography/mass spectrometry	Preselected hydrocarbons boiling range C_{4-30}	10^{-6} g.	GC/MS interface with digitizer and/or computer

Source: Based on background material presented in references [2], [4].

respect to the column liquid phase and to the type and resolution capability (packed, capillary, surface-support coated, etc.). The gas chromatograph can provide, in its simplest form, a "fingerprint" of the components in the sample; more detailed data, requiring additional expenditure of time, can provide substantial information on individual hydrocarbons which can indicate the origin of the materials. Any detailed study into petroleum uptake in marine organisms and in sediments should consider the incorporation of mass spectrometric identifications, especially in the use of computerized gas chromatograph/mass spectrometer systems. However, this tool should be used to complement existing methods which allow for more rapid and less expensive analyses of large numbers of samples.

The chemical composition and molecular weight range of the hydrocarbon fraction reported by whatever method used must be specific, such as n-paraffins, saturates, olefinics, aromatics, fluorescence materials, etc. It is also necessary to state the precision, accuracy, and the lower limit of sensitivity of the method used; one example of the latter using gas chromatography is given in table V under typical biogenic baseline operating conditions for n-paraffin hydrocarbons. Calibration of n-paraffins by routine gas chromatography can give a curve (fig.1) showing decreasing sensitivity with increasing carbon number so that calibrating a chromatogram at a single carbon number may lead to quantitative errors. Reproducibility and recovery of hydrocarbons added to biological samples should also be established. An example is given in an accompanying paper [9].

Table V. Typical lower detection limits by gas chromatography [a].

Carbon number	Routine [b]	Maximum
13	8	4
14	8	4
15	4	2
16	4	1
18	2	1
20	2	1
22	2	1
24	2	1
28	2	1
32	8	3
36	16	8

[a] Experimental conditions: Varian Aerograph model 1200; linear-programed temperature 6°/min., 60-332°C; hydrogen flame ionization detector; injector 300°C; detector 360°C; N_2 29 ml/min, H_2 28 ml/min; air 240 ml/min; 1.9 m. x 0.32 cm OD stainless steel column, 1.5% RTV 502 silicone rubber on Chromosorb G H.P., 80/100 mesh; 1 mv recorder 0.63 cm/min; automatic attenuator; instrument attenuator 8x on range 1 (8×10^{-12} amps).

[b] In nanograms, based on minimum peak area of 6 square units (1 unit = 0.02 inches).

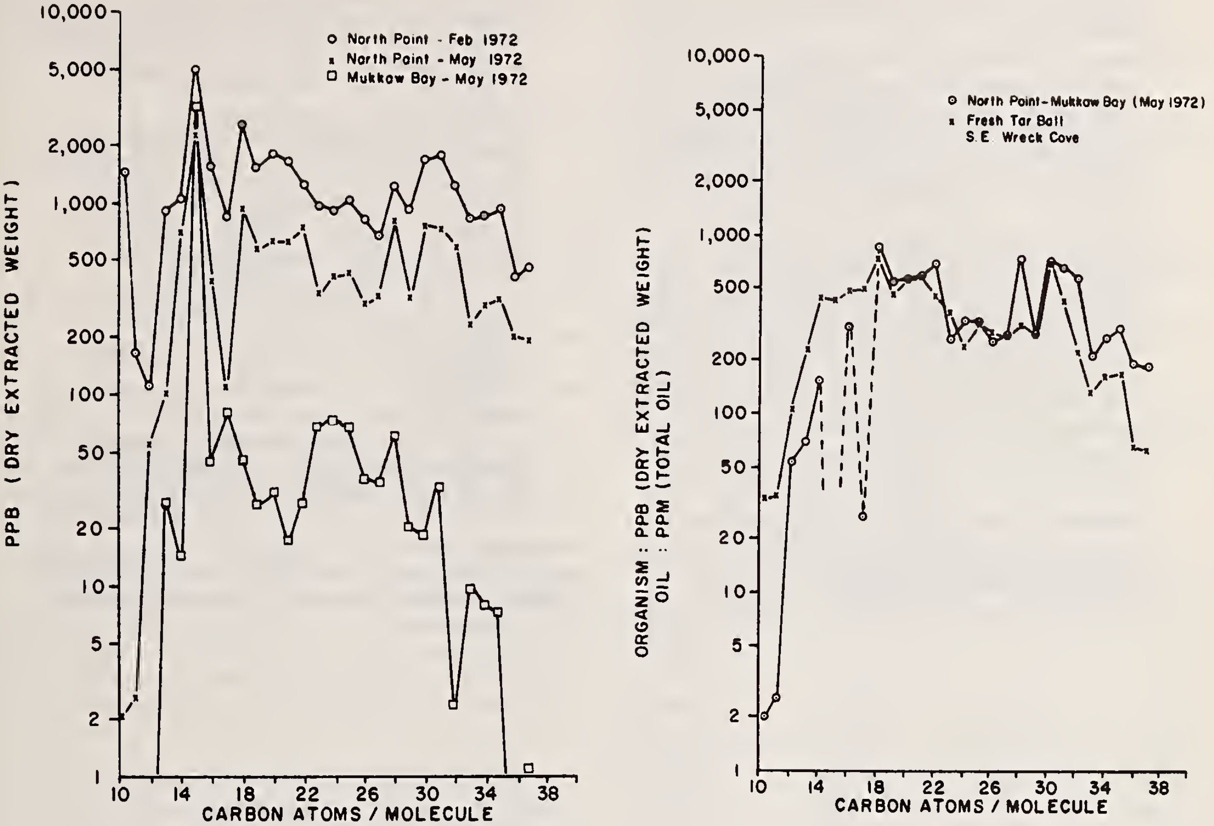

Figure 2. Paraffin hydrocarbon patterns for goose barnacles (Mitella polymerus) exposed to Navy Special Fuel Oil from the GENERAL M. C. MEIGS. A: Exposed samples compared with a control sample. B: The "residual" hydrocarbon pattern obtained by subtracting the control sample hydrocarbon values from the exposed is compared with the Navy Special Fuel Oil residue pattern [8].

Data Reduction

In an environmental monitoring program, it is ultimately necessary to indicate whether petroleum pollution has occurred and to what extent it has been incorporated into biological populations and sediments. An example of some of the numerical calculations that have been tried on paraffin hydrocarbons is given in an accompanying paper[9]. Other parameters which can be used on homologous series include the Odd-Even Predominance [10] and the calculation of "residual" hydrocarbon patterns (fig. 2 and [8], [11]).

Limitations

The absence of certain petroleum hydrocarbon classes in marine organisms does not necessarily prove the absence of petroleum pollution. In cases where the petroleum pollutant is low in paraffin hydrocarbons, paraffin hydrocarbon patterns may not be useful [7]. Aromatic hydrocarbons, which are a biogenic rarity yet often a major component in petroleum and its refined products, may be rapidly lost from contaminated organisms [12], [13], [14], [15] so their utility in marine pollution monitoring programs may be somewhat limited. These facts point out the need for research into the uptake, retention, and discharge of petroleum components by marine organisms before undertaking large-scale monitoring programs.

In order to plan a global pollution monitoring program for petroleum, we need to standardize sample collection, preservation and preparation, including a consistent scheme of sample weighing for marine organisms and sediments. We need to standardize extractive and chromatographic procedures and data reduction techniques so that the resulting data are compatible worldwide.

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Key Words: Analytical techniques, chromatography, hydrocarbons, marine organisms, oil pollution, paraffin residual patterns, petroleum contamination, sediments.

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QUANTITATIVE DETERMINATION OF HYDROCARBONS IN MARINE ORGANISMS

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Assessment of the extent and effects of contamination of the marine environment by petroleum fractions or crude oils requires a knowledge of the petroleum hydrocarbon uptake by marine organisms. Because of factors such as seasonal variations, discontinuous feeding habits, differences in life stages, specimen variability, and varying environmental stresses, numerous samples need to be analyzed in order to obtain reliable and meaningful results. The purpose of this paper is to describe reliable analytical methodology that is diagnostic for individual hydrocarbon components and applicable to the analysis of relatively large numbers of samples.

The procedure involves aqueous caustic digestion, ether extraction, silica-gel chromatography, and gas chormatography. Ten grams of homogenized tissue is mixed with four grams of 4N NaOH in a 50-ml screw-cap centrifuge tube and heated at 90 C for two hours. The digest is extracted with 25 ml of peroxide-free ethyl ether in two portions. The combined extract is concentrated to one ml, the ether is replaced by hexane, and the resulting hexane solution is cleaned up and fractionated by column chromatography using 0.9 x 25 cm column containing 10 g of silica gel activated at 150 C. Three fractions are collected. Fraction 1 is eluted with 25 ml of petroleum ether; fractions 2 and 3 are each eluted with 25 ml of 20 percent methylene chloride in petroelum ether. After adding 100 μg of n-dotriacontane as an internal standard each fraction is concentrated to 200 μl and a 2 μl aliquot is used for gas chromatographic analysis.

The method of concentration was found to be extremely critical if losses of naphthalene and similarly volatile components is to be avoided. The sample is contained in a 25-ml evaporator tube fitted with a modified Snyder column and concentrated by heating with a Kontes tube heater that is modified to permit heating from the bottom tip of the tube.

For the gas chromatography a 3.5 m x 2 mm I.D. glass column packed with 3 percent OV-1 or 3 percent OV-17 on 100-120 mesh Gas Chrom Q is used with the column temperature programmed from 60 to 300 C at 8 degrees per minute. Fraction 1 contains all of the saturated hydrocarbons; fraction 2 contains most of the mono- and diaromatic hydrocarbons as well as most of the biogenic olefins; and fraction 3 contains most of the tri- and polyaromatic hydrocarbons and and small amounts of biogenic olefins.

The recovery of hydrocarbons by this procedure was checked by analyzing oyster tissue to which known amounts of 1, 2, 3, 5-tetramethylbenzene, 2-methylnaphthalene, 2, 3, 6-trimethylnaphthalene, fluorene, phenanthrene, and n-tetracosane had been added. As shown by the data in table I which gives the averages of three determinations, recoveries were greater than 90 percent except at the 0.2 μg/g level.

Table I. Recovery of Hydrocarbons from Spiked Oyster Tissue

	AVERAGE % RECOVERY AT GIVEN LEVEL		
COMPOUND	10 μg/g	1 μg/g	0.2 μg/g
1,2,3,5,-Bz	97 ± 2	91 ± 5	68 ± 6
2-MN	99 ± 2	96 ± 4	74 ± 13
2,3,6-TMN	99 ± 1	99 ± 2	92 ± 3
Fluorene	95 ± 1	99 ± 2	95 ± 3
Phenanthrene	99 ± 2	94 ± 2	106 ± 5
C_{24}	95 ± 2	97 ± 1	100 ± 3

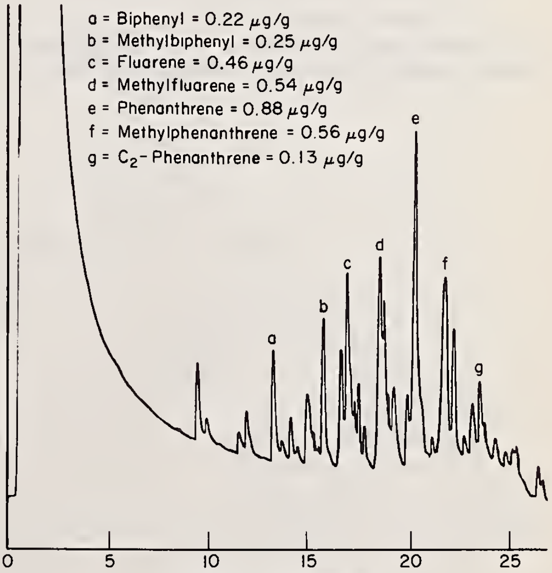

Figure 1. Gas Chromatogram of Fraction 3 from Clams Exposed to a Fuel Oil

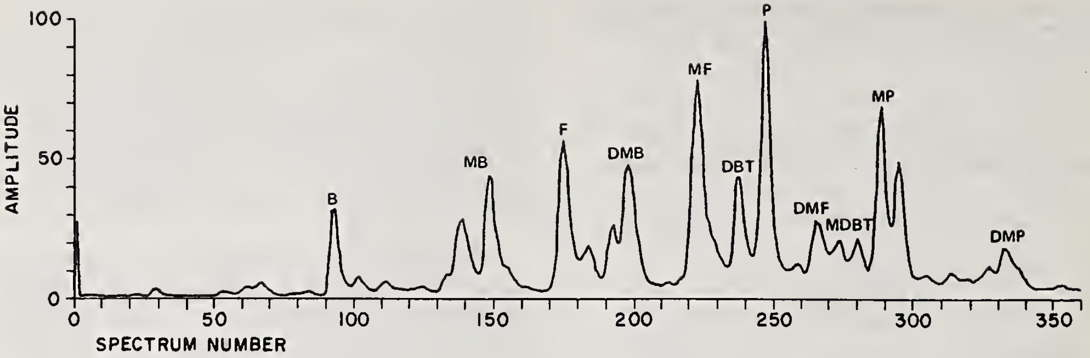

Figure 2. GC-MS of Fraction 3 from Clams Exposed to a Fuel Oil

Figure 1 is a representative gas chromatogram of a tissue extract containing low levels of hydrocarbons. This is a fraction 3 obtained from clams that had been exposed to a fuel oil.

The individual aromatic hydrocarbons were tentatively identified by using gas chromatography combined with chemical ionization mass spectrometry. The reconstructed gas chromatogram obtained by GC-MS of fraction 3 obtained from clams exposed to a relatively high level of a fuel oil is shown in figure 2. Biphenyl, fluorene, dibenzothiophene, and phenanthrene, and their methyl- and dimethyl-derivatives are indicated by the appropriate abbreviations.

We have used the overall extraction – gas chromatographic procedure on several hundred tissue samples including mussels, lobsters, clams, oysters, fish, shrimp, abalone, crabs, starfish, sea urchins, and bloodworms. Except for certain abalone viscera samples which contained high levels of interfering carotenoids, the method has been very satisfactory.

This work was supported by the American Petroleum Institute under Contract No. OS-20-G. Tissue samples were submitted by Prof. Jack Anderson of Texas A&M University under API Contract No. OS-20-C and Prof. Dale Straughan of the University of Southern California under API Contract No. OS-20-D.

Key Words: Aromatic hydrocarbons, gas chromatography, marine organisms, mass spectrometry, silica gel fractionation, tissue extraction.

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METHODS FOR TRACE ORGANIC ANALYSIS IN SEDIMENTS AND MARINE ORGANISMS

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The Prudhoe Bay area of Alaska is estimated to contain at least 10 billion barrels of crude oil. This crude oil is to be transported via pipeline to the ice-free port of Valdez on Prince William Sound, from which point it will be shipped via tanker to refineries and distribution facilities in the United States.

Tanker traffic, oil transfer, and ballast treatment facilities in Port Valdez are likely to increase current levels of hydrocarbons in the environment For this reason, a chemical baseline study (prior to the completion of the Alaskan Pipeline) of the aromatic hydrocarbon levels in sediment and marine organisms in the Prince William Sound area is in progress. It is the aim of this project to determine aromatic hydrocarbons at the part per billion (ppb) level. Aromatic hydrocarbons were chosen as petroleum indicators, due both to their supposed toxicity and to their insignificant biogenic levels.

A technique for the isolation and measurement of trace organics present on sediment has been developed and a similar technique for trace hydrocarbons in marine organisms is currently being developed. These techniques are the subject of this paper.

Experimental - The techniques and necessary precautions for the collection of samples (sediment, Fucus algae, mussels, and Macoma clams) from eight sites in the Prince William Sound are described by Bruce [1] in another paper presented at this meeting. Immediately after collection, the samples are quick frozen and transported in dry ice to the National Bureau of Standards, where they are stored at -50°C.

As part of the sample preparation procedure all glassware is first cleaned with soap and water and then placed in a hot concentrated sulfuric acid bath (100°C) for a period of at least 30 minutes. The glassware is then rinsed several times with house-distilled water and finally rinsed with specially prepared in-house water. This in-house water is also used in the sample analysis and is prepared by redistilling house-distilled water over $KMnO_4/KOH$. The distillate is then passed through a 90 x 2.5 cm column packed with XAD-2 [2] resin for final removal of any remaining traces of organic compounds. The water is then redistilled to remove particulates picked up from the XAD-2 resin. Reagents for the analysis of sediments include methanol, methylene chloride and n-pentane, and are singly or doubly distilled before use. When used, Soxhlet thimbles are pre-extracted with methanol & methylene chloride, to remove any organic contaminants which would subsequently interfere in the analysis. TENAX [3] pre-columns are flash-heated at 350°C for 20 minutes in order to drive off adsorbed organics.

The analysis scheme for sediments is outlined in figure 1. The method involves the headspace sampling by a stream of purified nitrogen and trapping on a TENAX pre-column in preparation for gas chromatography. The residual sample is then Soxhlet extracted with methanol followed by methylene chloride. The details of the analysis are described below. Normally, either six samples or five samples and a blank are run simultaneously.

Samples are thawed and transferred to the separation flask in a class 100 laminar flow, clean air hood located in

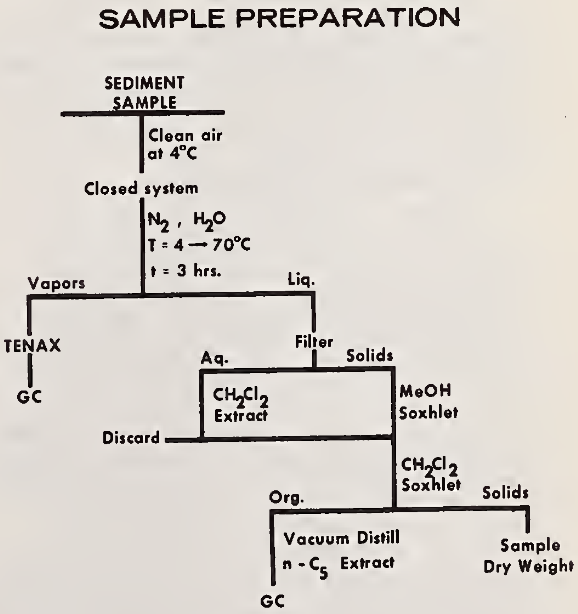

Figure 1. Analytical scheme for the preparation and analysis of sediment samples.

a cold room maintained at 4°C. Pure water (600 ml) and an internal standard containing several aromatic hydrocarbons (each at a concentration of 10 ppb) are added. The flask is then stoppered and transferred to an organic "clean lab" for sample extraction.

The flask is placed in a heating mantle mounted on a magnetic stirrer. One port of the flask is connected to the prepurified nitrogen line which directs a stream of gas across the liquid interface at a flow rate of ∿180 ml/min. A second port contains the exit line, which is connected to a 6 x 0.6 cm stainless steel Swagelock-fitted column packed with TENAX used for trapping the outgassed organics. This column is mounted in a cylindrical jacket which is chilled by a steady stream of cold air. Samples are outgassed for three hours, first at room temperature, and then while gradually raising the temperature to 70°C.

At the end of this period the nitrogen gas is diverted from the flask directly to the TENAX column for 2 hours in order to dry the column. The dried column is capped and taken to the instrument lab for analysis.

The residual sediment and water are then poured through a clean, dry, weighed Soxhlet thimble and the contents of the thimble extracted with methanol for 4 hrs. This step is necessary to switch from an aqueous to an organic solvent. The water is extracted with methylene chloride to remove any remaining organics in the aqueous phase. This methylene chloride is also used for further Soxhlet extraction of the sediment (20 hrs). The organic extracts are combined, reduced to dryness by vacuum distillation and taken up in n-pentane for gas chromatographic analysis. The solid residue in the Soxhlet thimble is used for dry weight determination.

The 6 cm. TENAX column from outgassing is installed as a pre-column to the analytical column in the gas chromatograph (GC). A heating block is clamped around the pre-column and heated to 400°C with carrier gas flowing. Just prior to and during this flashing operation, a stream of liquid nitrogen is directed at the head of the analytical column, thus thermally focusing the sample on the GC column. The oven is temperature programmed and data are acquired by an on-line computer throughout the course of the gas chromatogram. Data reduction routines are available for determining elution time and peak size. Identification of the components trapped on TENAX will be accomplished with a gas chromatograph-mass spectrometer system.

The analytical columns used in the gas chromatograph are glass SCOT columns 100 m in length x 0.76 mm i.d., drawn and coated in this laboratory. They are coated with SE-30 on Silanox 6-10μ silica particles. The columns exhibit more than 100,000 theoretical plates.

The analytical scheme under investigation for tissue samples is similar to the method described above. Prior to the outgassing, an ultrasonic probe is introduced into the extraction flask through a normally stoppered neck and the cell structure is disrupted. Since no solid mass remains, the analytical procedure is not carried beyond the outgassing stage.

Results and Discussion - As mentioned above, for tissue samples only the outgassing step is envisioned. Results of sediment studies show that aromatic hydrocarbons such as pyrene (molecular weight 202) can be outgassed. This result indicates that also for sediments Soxhlet extraction may not be necessary. Typical chromatograms for outgassed sediment samples from two of the sampling sites in Prince William Sound are shown in figure 2. The Dayville mud flats (clay-type sediment) are located across the channel from Port Valdez at the head of the Prince William Sound, in reasonably confined waters. Hinchinbrook Island (sandy sediment), on the other hand, is located outside the Valdez arm at the entrance of the Sound into the Pacific Ocean, and hence its beaches are constantly washed with new ocean water. Peak 1 is pentane, the solvent for the internal standard. Peaks 2, 3, 4, and 5 are the components of the internal standard, each added at the 10 ppb level based on sediment wet weight. As can be seen (Dayville sediment), pentane, due to its great volatility, is difficult to retain on TENAX. The Hinchinbrook sediment, as might be expected, is much cleaner than that of Dayville.

The advantages of the outgassing and trapping technique for sample analysis over the more classical solvent extraction and column chromatography techniques are considerable:

1) There is an absolute minimum of sample handling.
2) Separation is in a closed system minimizing both the risk of losses of trace level volatile constituents and the possibility of contamination by laboratory vapors and particulates.
3) The method affords efficient separation and concentration of the constituents of interest.
4) Only water is added to the

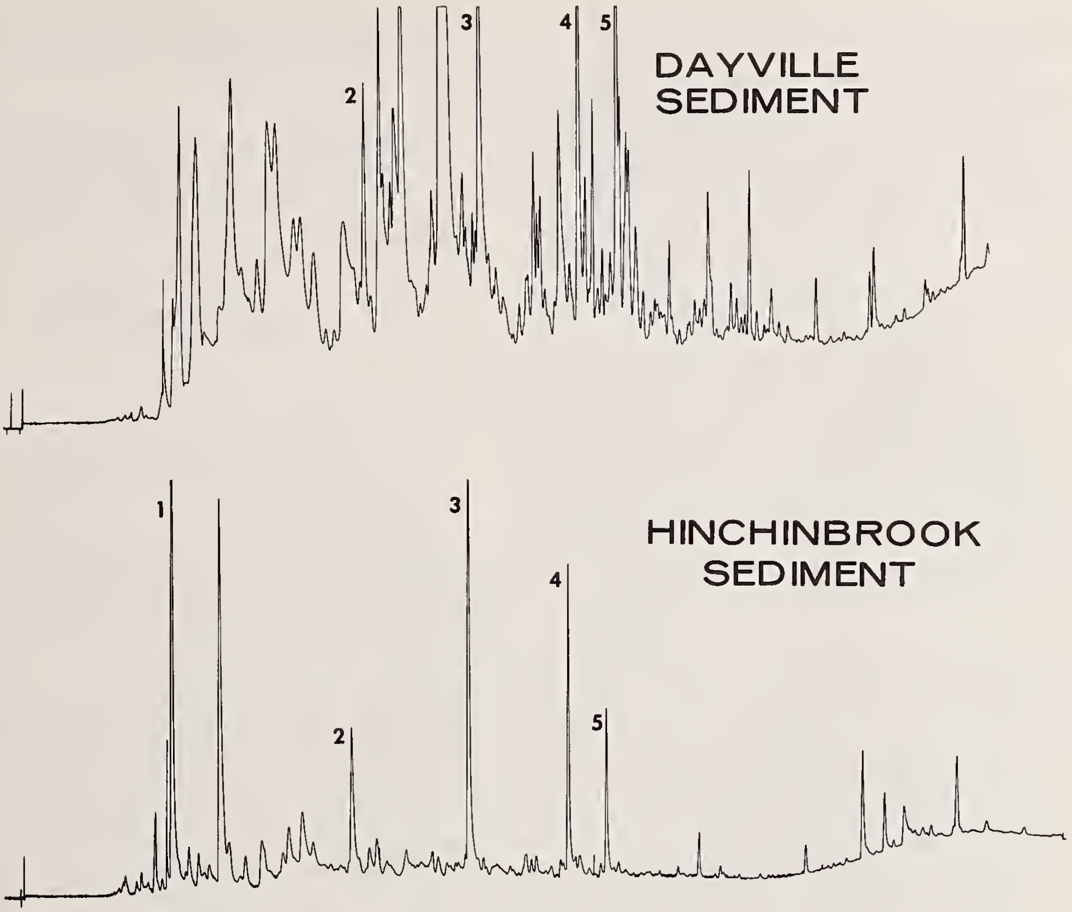

Figure 2. Gas chromatograms of outgassed sediment samples from Dayville Mud Flats and Hinchinbrook Island, Prince William Sound, Alaska. Peaks 1 through 5 are due to the internal standard and correspond to: (1) n-pentane, (2) mesitylene, (3) naphthalene, (4) ethylnaphthalene, (5) n-propylnaphthalene.

sample - water can be purified to a higher degree of purity and much more readily than organic solvents.

5) The sample ends up in a form which can be readily chromatographed, free of large amounts of solvents and free of septum bleed.
6) Even reasonably nonvolatile hydrocarbons, such as pyrene (molecular weight 202) and docosane (molecular weight 310) can be outgassed.

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[2] XAD-2, a product of Rohm and Haas Company, Philadelphia, Pa. XAD-2 is a copolymer of polystyrene-divinylbenzene.

[3] TENAX^{R} - GC is a registered trademark of Enka N.V. The Netherlands. Tenax GC is a porous packing material based on 2, 6, diphenyl-p-phenyleneoxide.

Key Words: trace analysis, hydrocarbons, aromatic hydrocarbons, chemical baseline, gas chromatography, Prince William Sound.

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LONG TERM WEATHERING CHARACTERISTICS OF IRANIAN CRUDE OIL: THE WRECK OF THE "NORTHERN GULF"

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On November 25, 1963, the Liberian tanker Northern Gulf ran aground on West Cod Ledge, Casco Bay, Maine, with a loss of approximately 5,000 metric tons of Iranian crude oil. The weather was clear; northwest winds averaged 17.6 km. per hour, with a peak gust of 46.4 km. [1]

Much of the oil was rafted eastward by an anomalous clockwise eddy [2] to the vicinity of lower Penobscot Bay where a southeast gale on November 30 drove the oil ashore along more than 64 km. of coast. The beach area occupied by the stranded oil between extreme low tide and above mean high tide was estimated to be approximately 1.6 km^2.

All commercial shellfish growing sites, principally soft clam (Mya arenaria), were contaminated by the oil. One regularly sampled soft clam growing area could not be harvested for a period of two years following the spill. In this period the supply of marketable clams from the affected areas declined 20 percent, or 60 metric tons of edible meats, as contrasted with an increase of 249 percent or 157 tons in adjacent uncontaminated control areas. Most of the loss was caused by unpalatable oily flavor apparently imparted by repeated or continuous recontamination by oil entrapped in bottom sediments. Following the immediate toxic effects [3] the persistence of the Iranian crude oil entrapped in bottom sediments would appear to have played a significant but not exclusive role in the continuing mortalities observed in these areas during the subsequent two-year period. These results are in contrast to the virtually instantaneous mortalities associated with some fuel oil spills observed elsewhere on the Maine coast.[4] The total two-year market loss of clams from the spill is estimated to have been between a minimum of 60 and a probable maximum of 209 metric tons of edible meats.

Within the spill area were located five tidal storage impoundments, containing approximately 647,000 lobsters (Homarus americanus). The largest of the lobster impoundments, located on Long Island in Friendship, Maine, contained approximately 300,000 lobsters. Immediate losses of 28,800 lobsters, weighing 15.2 metric tons, were reported by three of the impoundment operators.

The dam enclosing the cove to create the impoundment prevents contamination by an outside oil spill except under abnormal meteorological conditions. Those conditions were satisfied as the storm which brought the oil into the Friendship impoundment on November 30, 1963, was reported by the U.S. Weather Bureau to have been from the south with an average wind velocity of 44.8 km/hr, a maximum of 76.8 km/hr, and a peak gust of 121.6 km/hr. [1] During the preceding day, the wind had been from the southeast, with a maximum speed of 49.6 km/hr and a peak gust of 65.6 km/hr.

The Long Island lobster impoundment has been checked periodically following this initial contamination for visible evidence of oil residues. It is located in a rather isolated area which has not been exposed to subsequent spills. On surficial intertidal fine sediments, however, oil still persists as a visible sheen and in subsurface sediments as entrapped residues, with a strong oily odor when samples of sediments and of soft clams are collected.

As there had been no recorded evidence of either prior or subsequent contamination of this area by petroleum hydrocarbons, a study was commenced during the summer of 1972 to establish the present state of the hydrocarbon residues in the sediments and marine life of this area resulting from the wreck of the Northern Gulf. The hydrocarbon content of the area was assayed by gas chromatography employing a Perkin-Elmer model 900 instrument equipped with a SCOT 50' OV-1 column. Generalized parameters for instrument operation are given in reference [5]. Sampling procedures for sediments and organisms were essentially those outlined by Blumer. [6] The resolution capability of the OV-1 open tubular columns will allow (with careful handling) nearly total separations of the acyclic isoprenoid series from C_{14} to C_{20} while at the same time giving complete separation of all the linear chain compounds. This result is observed in figure 1 (sample C-1) where the gas chromatogram of the original unweathered Agha Jari crude carried by the Northern Gulf is shown. Of particular interest was an area in the northwest corner of the pound where deep penetration of fine sediments had occurred nearly ten years prior to the start of current studies.

Samples A1 and A2 (fig. 1) collected in June of 1972 and March of 1973 possessed particularly interesting chromatograms. Both samples were subsurface and were essentially devoid of linear chain hydrocarbons (traces present in A2). The branched chain series still persists in these hydrocarbon residues. With the exception of pristane the same relative abundance of C_{14} through C_{20} isoprenoids is observed (see Table I) with respect to the unweathered Agha Jari crude. In the unweathered oil the C_{16} member occurs in highest concentration, whereas in the sediments pristane dominates the isoprenoid fraction. It would appear that during the weathering of the crude oil pristane is being degraded much more slowly than the six other members of this series. An alternative explanation is that pristane is being incorporated into the residues from the natural environment. Substantial evidence has been found to support the latter contention. Indeed, it would seem that sediments located within lobster impoundments may tend to exhibit unusually high natural pristane concentrations. This conclusion arises from the observation that in assaying lobsters for hydrocarbon contamination all control animals without exception possessed pristane as the single dominant hydrocarbon (see sample B3a, fig. 2). Thus, in a pound containing over 300,000 lobsters/year and with a storage mortality of approximately 5 to 8% it would be anticipated that rather high natural pristane levels would develop over a period of years. Indeed, in the northeast corner of the pound in surface sediments which contained significant contamination but which were more highly weathered so that the isoprenoid series was reduced to trace quantities, the single exception was pristane which was again the dominant hydrocarbon (see sample A6, fig. 2). Even in clams collected within the pound pristane is the dominant saturated hydrocarbon (see sample B2, fig. 2).

Table I. Ratios of Isoprenoids Relative to Phytane

Isoprenoid	Iranian Crude	Friendship Sediments		
		Sample		
		A1(72)	A2(73)	A9(74)
C_{14}	0.8	0.3	0.3	0.2
C_{15}	0.8	0.7	0.7	0.5
C_{16}	1.2	1.2	1.3	1.2
C_{17}	0.7	0.6	0.5	0.7
C_{18}	1.0	1.0	1.0	0.9
C_{19}	1.0	1.8	1.7	1.9
C_{20}	1.00	1.00	1.00	1.00

Thus, by correlating the relative abundance of the isoprenoid substances we may conclude with reasonable confidence that the hydrocarbon residues which still are present in the impounded area eleven years following the spill can be traced to the Northern Gulf.

Background distributions of hydrocarbons from sediments adjacent to the impounded area are given in figure 3. Subsurface beach sediments collected south of the pound (sample A7) still show moderate contamination of heavily weathered material. Sediments obtained from a fresh water bog draining into the pound but not contaminated during the spill exhibit a rich distribution of natural hydrocarbons but no indication of petroleum residues (see fig. 3, sample A5).

Organisms living in the area also reflect the presence of these residues. A sample of fucus collected during July of 1973 possessed lower concentrations, but the same isoprenoid distribution (sample D1, see figure 4). Heavy concentration of aromatic residues in this plant also appears to have taken place.

Clams surviving in the northwest corner of the pound possess a hydrocarbon distribution essentially identical to the sediments in which they were found (sample B4, see fig. 4).

The clams occupying this area of the pound are stunted, requiring eight or more growing seasons to reach the minimum commercially acceptable size of approximately 45 mm long diameter. By comparison the most rapidly growing clams in Maine will reach market size in three growing seasons and the coastwide average is five.

Although water circulation is inadequate in this portion of the impoundment for good growth, it is probably less important than the chronic effects of the high level of petroleum hydrocarbons in the sediments where the clams live. Estimated annual linear growth has averaged 5.6 mm with a range from 3.6 to 8.2 mm. Although representation in the samples was limited to approximately eight year classes, nearly four percent of the residual population in 1973 had apparently been spawned during the summer preceding the spill.

To evaluate further the effects of oil residues on clams, two clam-transplanting experiments were conducted. On June 20, 1973, 1,805 soft shell clams ranging in long diameter from 44 to 89 mm were planted behind the dam of the Long Island impoundment on the Northwest shore. It was estimated that the area included in the planting consisted of approximately 35 m^2. 2032 similar size clams were replanted as controls in the Spurwink River, Scarboro, Maine, using the handle of a clam hoe to create artificial burrows. The Scarboro control area contained approximately 24 m^2 of sand-silt sediments.

Nine hundred of the clams used in the Friendship planting were inserted approximately one-half the length of their shells in the sediments in normal growing position. The remaining 905 clams were placed in normal position in burrows excavated in the sediments by means of a garden trowel. Since these two lots were not placed in the same portion of the study plot, it was possible to differentiate them geographically.

When the first recovery sampling was made on July 23, all of the clams which had been partially inserted in the sediments were dead. Continuing survival of the remaining 905 is shown in Table II. At the time of the November 9 sampling, 142 days following the transplant, only two clams survived. The total mortality for this experiment was 87.4 percent in contrast to a total mortality of 13 percent in the control area when that experiment was terminated on October 22, 1973.

Only 319, both living and dead, of the 905 clams placed in excavated burrows were recovered, suggesting that the remaining 586 may have surfaced and died as occurred at Searsport, Maine, in March 1971 when a spill of #2 fuel oil mixed with JP5 killed approximately four and one-half million commercial size clams in less than two weeks. [4]

The surface of the experimental area in the Friendship lobster pound was littered with the empty shells of those transplanted clams that failed to burrow to their normal depth and those which, it is presumed, surfaced from their excavated burrows.

A second experimental transplantation of three hundred rapidly growing 30 mm diameter clams from Ogunquit, Maine, was made at Friendship on August 23, 1973. These animals were implanted in the oil-contaminated sediments at normal depth and in normal growing position. When the first recovery collection was made on September 21, only four living clams could be found. The mortality rate for the 29-day period was 99 percent, while in the control area the mortality during the same period was 40 percent.

Hydrocarbon sampling of the transplants and controls indicated that there was a rapid absorption of hydrocarbon residues by the surviving animals at Friendship (see Table III).

Table II.

Place	Date Planted	Number Planted	Date Collected	Number Collected	Number Alive	Number Dead	Percent Survival
Friendship	June 20	1805*	July 23	93	75	18	80.6
			Aug. 23	94	75	19	79.8
			Sept. 21	111	75	36	67.6
			Nov. 9	21	2	19	9.5
Scarboro (Control)	June 18	2032	July 16	83	75	8	90.4
			Aug. 23	82	75	7	85.3
			Sept. 20	83	75	8	90.4
			Oct. 22	96	75	21	78.1

*Nine hundred clams failed to reestablish themselves in burrows and were dead when the experimental area was checked on July 23, 1973.

Table III. Hydrocarbon Uptake by Transplanted Clams

Code #	Description of Sample	Date Collected	PPM - Total HCs
OTP-B-1	Marked clams from Spurwink-standard sample on day of collection.	6/17/73	12
OTP-B-4	Spurwink transplants used as standard at Spurwink.	7/23/73	8
OTP-B-12	Same as OTP-B-4	8/23/73	2
OTP-B-14	Same as OTP-B-4	9/21/73	3
OTP-B-2	Spurwink transplants from Friendship (inside lobster pound--northwest shore)	7/23/73	64
OTP-B-6	Same as OTP-B-2	8/23/73	88
OTP-B-10	Same as OTP-B-2	9/21/73	81

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[1] "Local Climatological Data." U.S. Dept. of Commerce, Weather Bureau, Portland, Maine. November 1963.

[2] "Coastal Currents of the Western Gulf of Maine," Joseph J. Graham, International Commission for the Northwest Atlantic Fisheries, Research Bulletin, #7, 1970.

[3] M. Blumer and J. Sass. Unpublished manuscript, reference 72-19, Woods Hole Oceanographic Institution 1972.

[4] "Final Report, Searsport Oil Spill Survey," Department of Sea and Shore Fisheries, Augusta, Maine 1972.

[5] Injection block temperature 200°C; Detector: Flame Ionization (400°C); Carrier Gas: Helium, flow rate 70 second methane retention time; Initial temperature 70°C; Final temperature 255°C with a 24 minute hold; programmed temperature at 6°/minute, recorder speed 18 inches/hr.

[6] Blumer, M.G. Sonza and J. Sass, Hydrocarbon Pollution of Edible Shellfish by an Oil Spill, Reference No. 70-1, Woods Hole Oceanographic Institution, 1970.

Key Words: Oil Pollution; Gas Chromatography, SCOT Columns, Isoprenoids, Weathered Oil, Oil Absorption, Organisms, Sediments

FIGURE 1

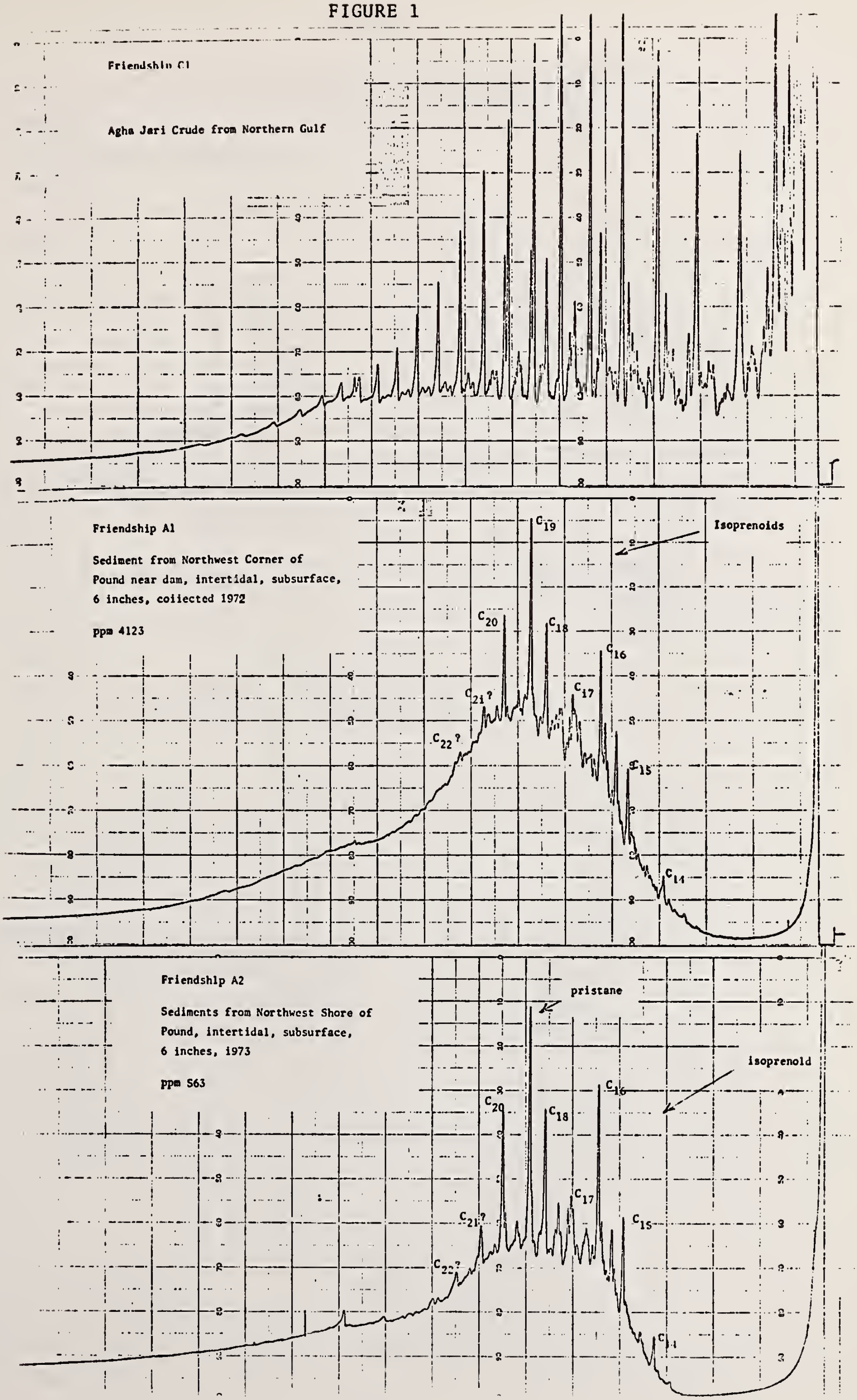

Friendship C1
Agha Jari Crude from Northern Gulf
Friendship A1
Sediment from Northwest Corner of
Pound near dam, intertidal, subsurface,
6 inches, collected 1972
ppm 4123
C_{19}
Isoprenoids
C_{20}
C_{18}
C_{16}
C_{21}?
C_{17}
C_{22}?
C_{15}
C_{14}
Friendship A2
Sediments from Northwest Shore of
Pound, intertidal, subsurface,
6 inches, 1973
ppm 563
pristane
isoprenoid
C_{20}
C_{18}
C_{16}
C_{17}
C_{21}?
C_{15}
C_{22}?
C_{14}

FIGURE 2

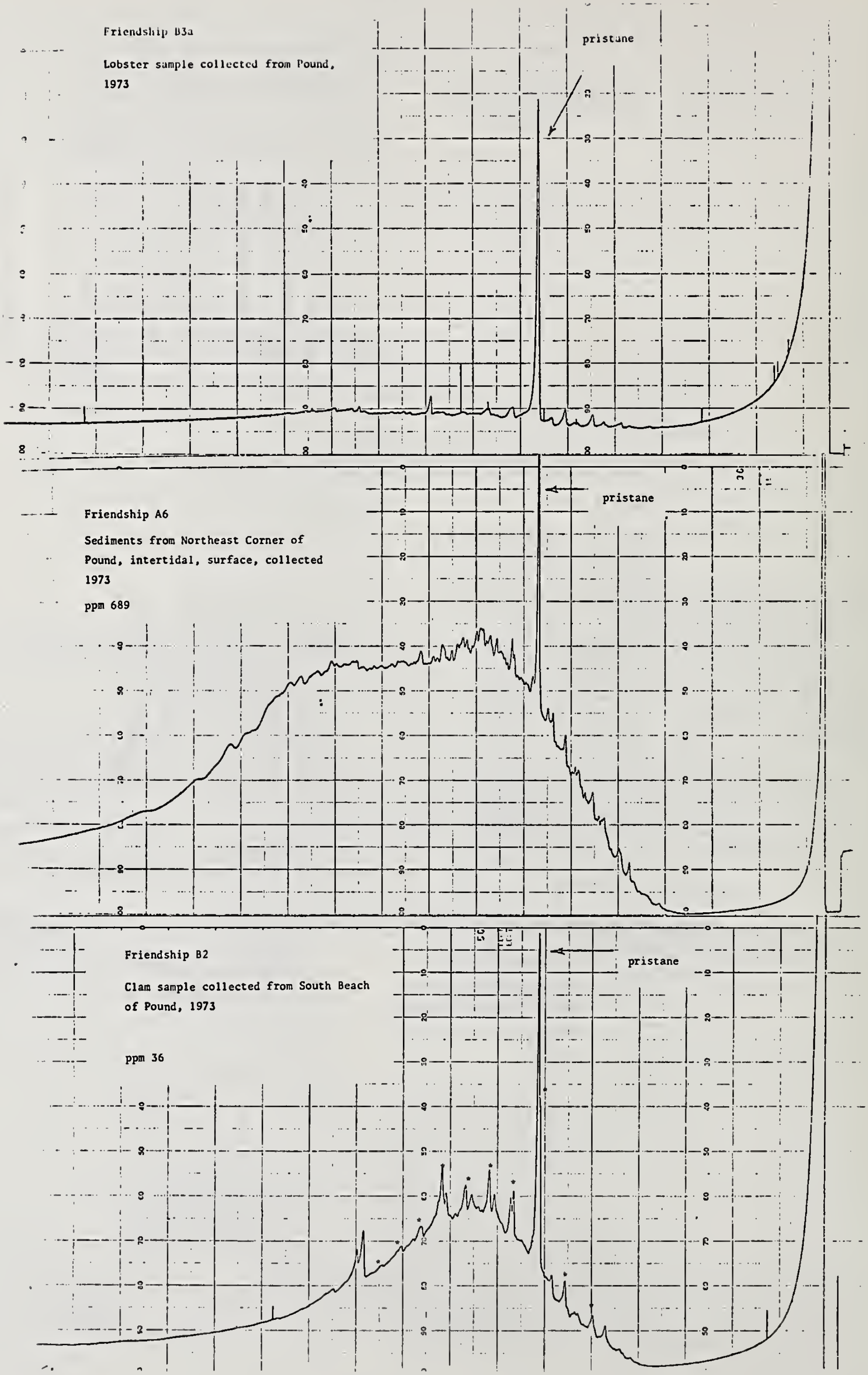

Friendship B3a
Lobster sample collected from Pound, 1973
pristane
Friendship A6
Sediments from Northeast Corner of Pound, intertidal, surface, collected 1973
ppm 689
pristane
Friendship B2
Clam sample collected from South Beach of Pound, 1973
ppm 36
pristane

FIGURE 3

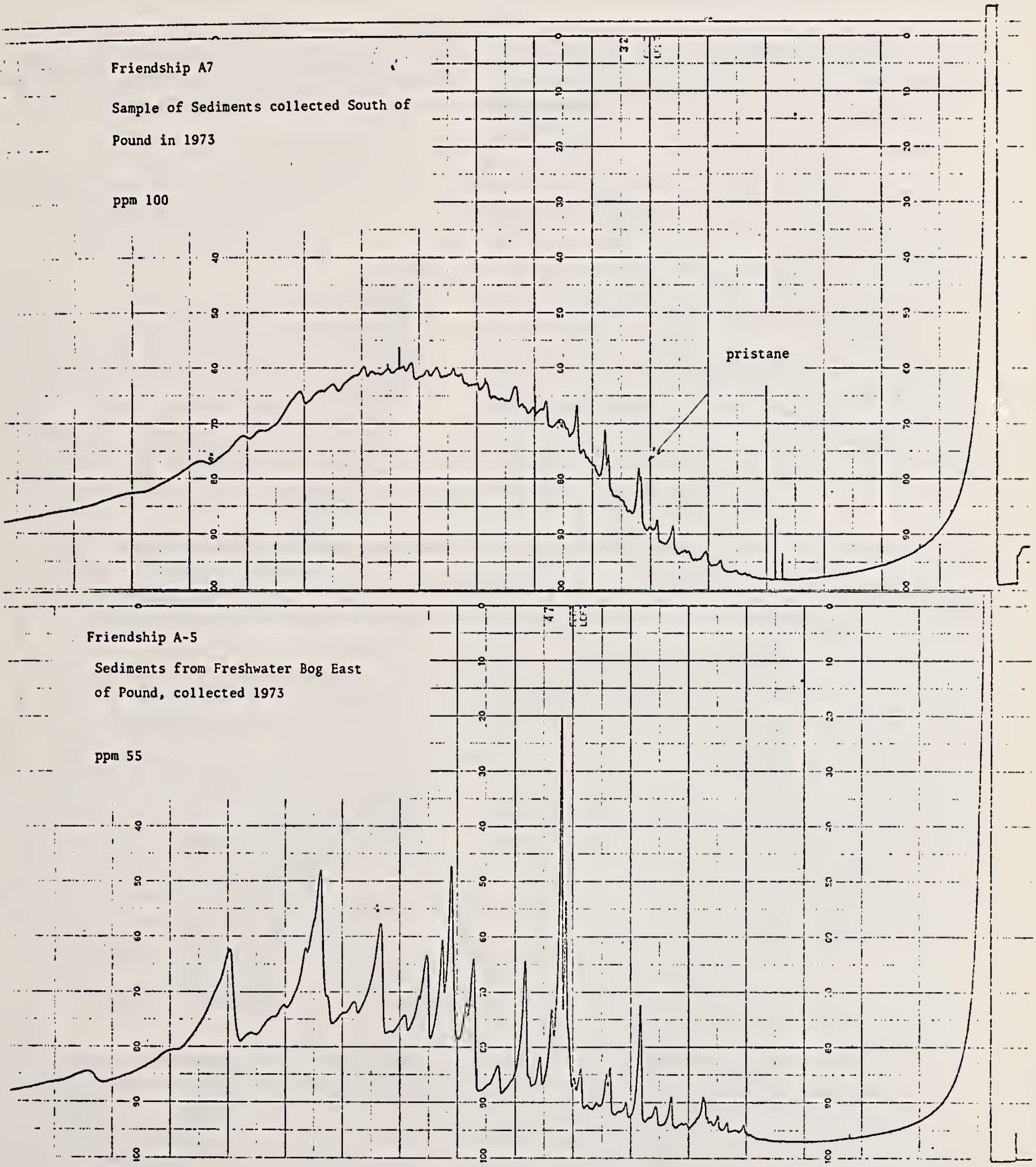
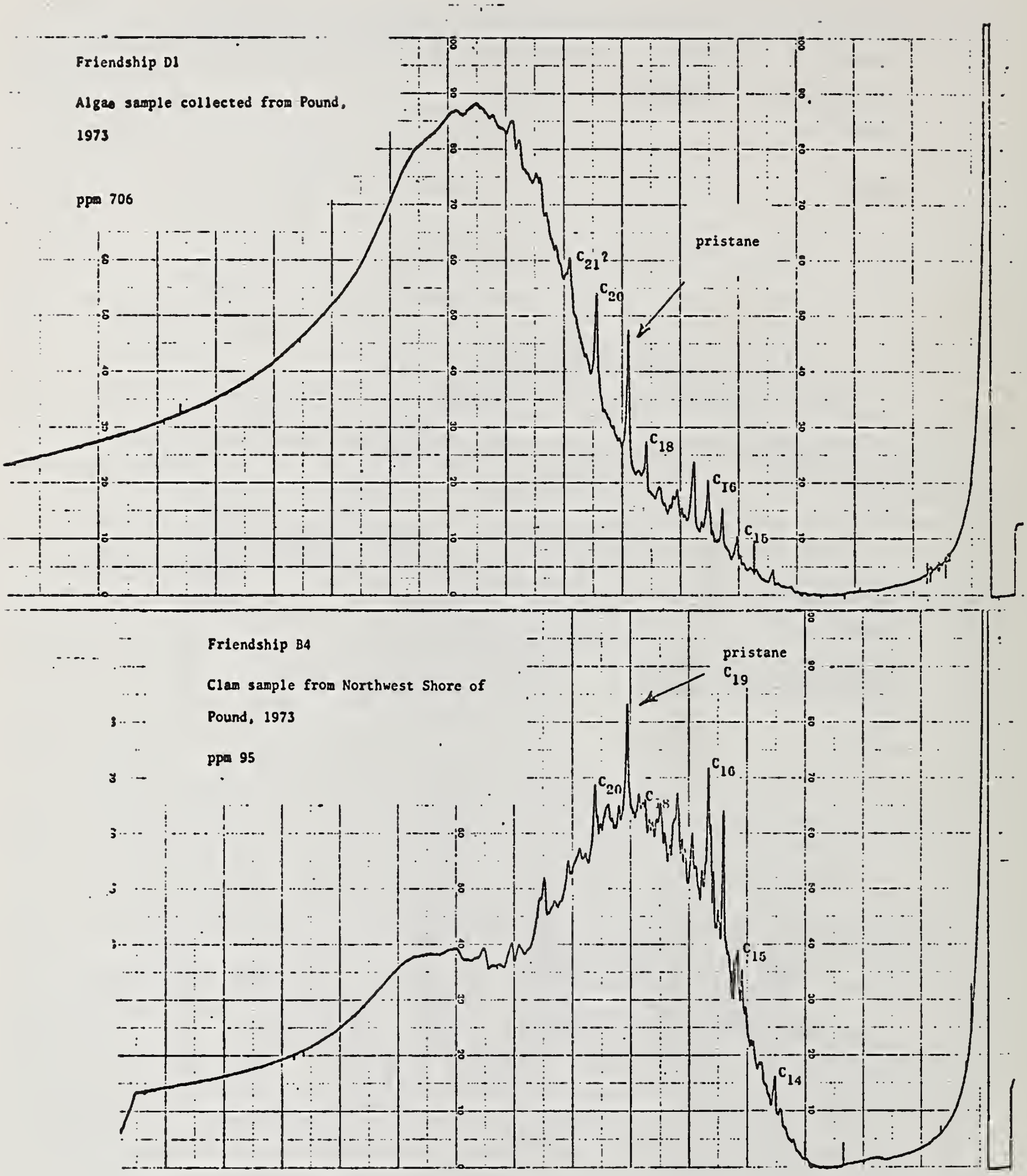

Friendship A7
Sample of Sediments collected South of
Pound in 1973
ppm 100
pristane
32
Friendship A-5
Sediments from Freshwater Bog East
of Pound, collected 1973
ppm 55
47
10
20
30
40
50
60
70
80
90
100

FIGURE 4



Friendship D1

Algae sample collected from Pound, 1973

ppm 706

Friendship B4

Clam sample from Northwest Shore of Pound, 1973

ppm 95

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ANALYTICAL TECHNIQUES FOR ISOLATING AND QUANTIFYING PETROLEUM PARAFFIN HYDROCARBONS IN MARINE ORGANISMS

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Straight-chain saturated hydrocarbons (normal paraffins or n-alkanes, C_nH_{2n+2}) are one of the major components of petroleum and of its refined products as well as being minor but ubiquitous compounds in the aquatic environment. They occur in aquatic organisms, in sediments, and in sea water itself. Since these compounds can be readily separated using liquid-solid chromatography and easily identified by gas-liquid chromatography, normal paraffin hydrocarbons can be used as tracers or indicator compounds for petroleum pollution.

Normal-paraffin hydrocarbon patterns in petroleum-contaminated marine organisms can be distinguished from those of biogenic origin within the same organisms by means of specific analytical techniques. Benzene-methanol solvent extraction, silica gel-alumina column chromatography, and linear programmed-temperature gas chromatography are used to isolate and identify individual n-paraffin hydrocarbons at the nanogram (10^{-9} g) level over the molecular range from 14 to 37 carbon atoms. Peak area quantification can provide a method for the preparation of n-paraffin hydrocarbon data to indicate (1) whether petroleum hydrocarbons have been taken up by marine organisms, and (2) to what extent this is the case. The applicability of these techniques has become evident from the results of several hundred analyses involving nearly 100 different types of plant, animal, petroleum, water, and sediment samples collected under conditions of low, moderate, and high level petroleum pollution.

Procedures to Isolate and Identify Paraffin Hydrocarbons

There are four basic phases in the isolation and identification of paraffin hydrocarbons in aquatic organisms:

(1) preparation of samples in a non-contaminating manner;
(2) solvent extraction of the organic matter from the cellular matrix of the samples;
(3) separation of paraffin hydrocarbons from the extractable organic matter by chromatography; and
(4) identification of the paraffin hydrocarbons by gas chromatography.

Specific details of the procedures used have been described [1] and its application to a number of petroleum-polluted and control intertidal organisms have been presented [2],[3],[4]. A flow diagram of analysis of paraffin hydrocarbons in marine organisms is given in figure 1.

Techniques for Interpretation of Data

Since the methods of hydrocarbon analysis of biological samples are relatively new, the procedures for making the data meaningful are in a developmental stage.

Once the organisms have been sampled and analyzed and the gas chromatograms obtained, it becomes necessary to interpret the results by preparing paraffin hydrocarbon patterns for each sample. Further calculations of parameters from the quantitative data can be made. A number of these parameters which by themselves imply pollution, can, in combination, delineate the extent of petroleum pollution in aquatic organisms. Finally, when sufficient basic information has been established (baseline patterns, bioassay uptake patterns, control patterns, etc.) in the form of paraffin hydrocarbon patterns and calculated parameters, then it becomes possible to apply this data for the detection and following of the uptake of petroleum hydrocarbons by marine organisms.

Paraffin Hydrocarbon Patterns

Regardless of the gas chromatograph used, the paraffin hydrocarbon pattern is depicted as a series of spikes on a potentiometric strip chart recorder (fig. 2). The resulting "chromatogram" from the recorder is qualitative, but it requires further interpretation to become quantitative. If one assumes that the area under the individual paraffin peak is directly related to concentration, the absolute weight value (expressed as nanograms) can be obtained using the proper calibration solutions, solvent blanks, dilution factors and peak area quantification. The division of this weight value by the "dry extracted weight" (sum of the solvent extractables and the "dry residue" weights), results in a "parts-per-billion" value which can be plotted on semi-logarithmic graph paper, against the number of carbon atoms per molecule along the abscissa in the form of a smooth line graph (fig. 3) for easy comparison of several patterns or "fingerprints" on a single chart.

Calculation of Parameters

There are several parameters which can be calculated from the quantitative data obtained during the preparation of paraffin hydrocarbon patterns. As parameters that can be used to indicate petroleum pollutant uptake in aquatic organisms, the solvent extractables, the total normal paraffin hydrocarbon content, the pristane content and n-C_{17}/pristane ratio, the magnitude of the major hydrocarbon, the n-C_{16} ratio, the carbon preference indices (CPI's) and the unresolved peaks envelope are useful to varying degrees.

Application of Data

The first indication of petroleum being taken up in aquatic organisms can often be seen in the gas chromatogram of the sample. If each of the n-paraffin peaks in the range C_{12-22} are of the same order of magnitude, and if there is a large

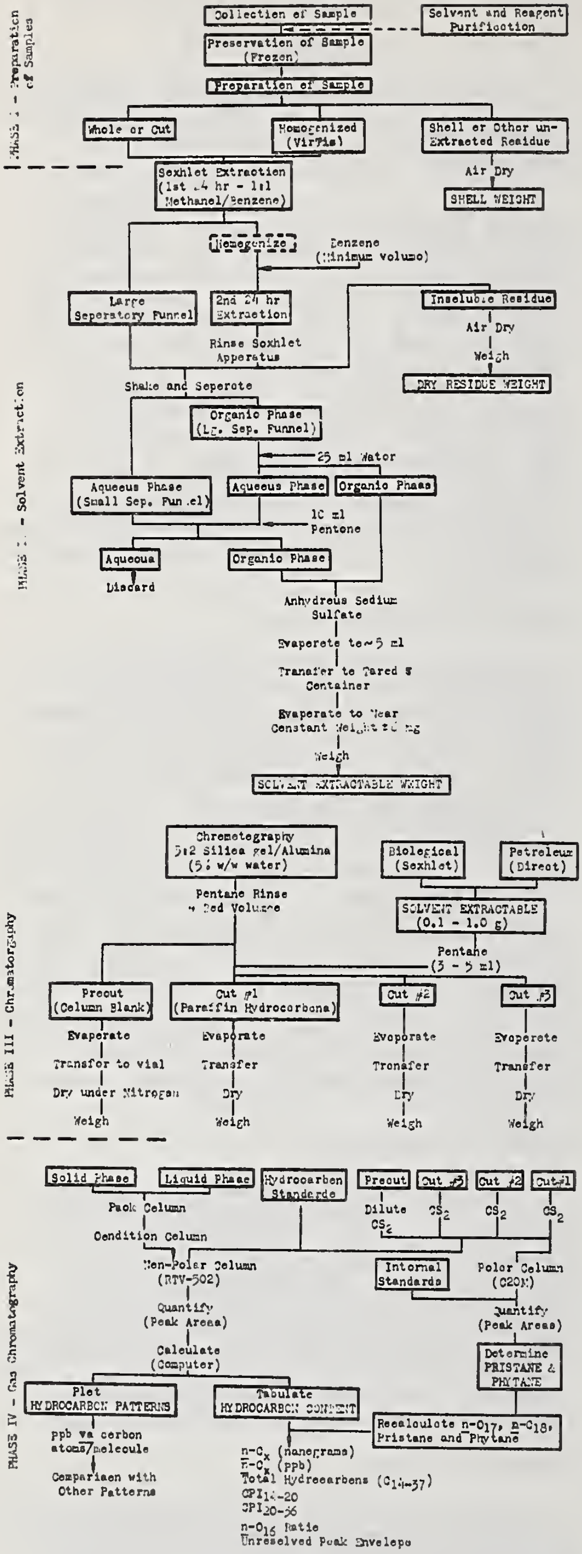

Figure 1. Flow diagram of analysis of paraffin hydrocarbons in marine organisms.

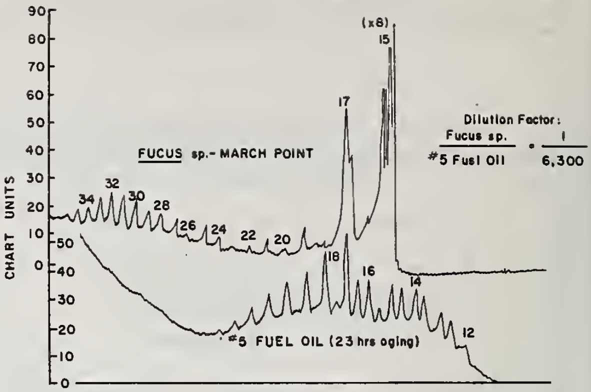

Figure 2. Gas chromatogram of extracts from an alga (Fucus sp.) and a petroleum product (#5 fuel oil). Sample size adjusted to show minimum attenuation for graphic presentation; the petroleum pattern represents a dilution of 1/6300 times that of the alga pattern.

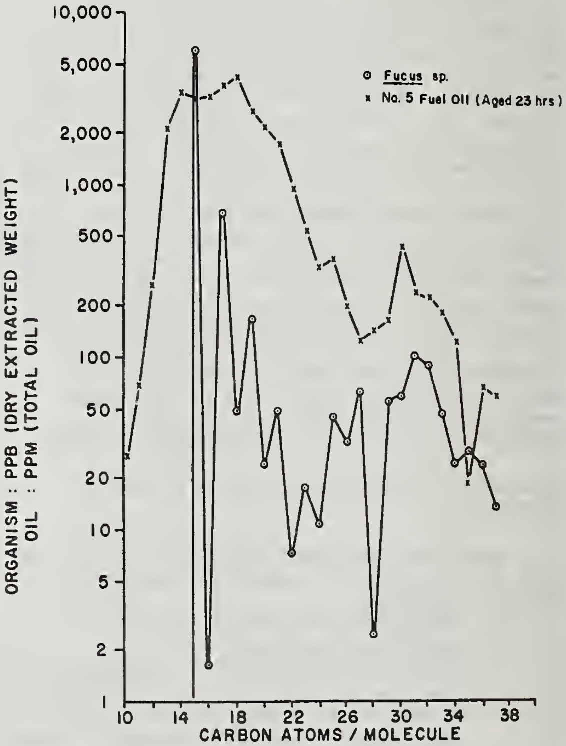

Figure 3. Line graph used for comparing paraffin hydrocarbon patterns. An alga (Fucus sp.) with its saw-toothed odd-carbon pattern representative of biogenic samples is compared with a #5 fuel oil which displays the smooth pattern found in petroleum samples.

unresolved peak envelope below the discrete paraffin peaks, a strong probability exists that the sample is contaminated with a petroleum pollutant.

The next step in establishing the levels of petroleum pollution uptake is then the converting of the peak areas from the gas chromatogram to the "ppb-dry extracted weight" value for each n-paraffin hydrocarbon and replotting (fig. 3). If the resulting pattern and content is indicative of petroleum contamination when compared with patterns of uncontaminated organisms and of petroleum materials, further reduction of the data is suggested.

As a start to using normal paraffin hydrocarbon baseline data obtained by the techniques outlined above, the following sequence might be considered:

(1) obtain a gas chromatogram at maximum sensitivity;
(2) reduce gas chromatogram peak data to "ppb-dry extracted weight";
(3) plot the "ppb" information on semi-log paper ("fingerprint");
(4) compare "fingerprints" of suspected organisms with unexposed controls and with petroleum;
(5) calculate: solvent extractables
    total normal paraffin hydrocarbons
    n-C_{17}/pristane ratio
    CPI_{14-20}
    CPI_{20-36}
    unresolved peak envelope ratios;
(6) calculate "residual" hydrocarbon patterns by subtracting the unexposed control patterns from the suspected or exposed patterns--positive "residual" patterns in the shape of the pollutant pattern indicate hydrocarbon uptake;
(7) compare the above calculations for trends and for an estimate of petroleum pollution.

As an example, the n-paraffin hydrocarbon patterns of an alga and a refined petroleum product obtained as gas chromatograms (fig. 2) are presented in PPB-Dry Extracted Weight pattern (fig. 3) and summarized in table I. Application of these techniques to other organisms and to various pollution exposures have been reported [2],[3],[6].

Table I. Parameters calculated from n-paraffin hydrocarbon data for *Fucus* sp. and for a #5 fuel oil. Data from figure 3.

Parameter	*Fucus* sp.	#5 fuel oil
Solvent extractables (ppm)	54,000	100%
Total paraffin hydrocarbons (ppm)	7.217	29,057
n-C_{17}/ pristane ratio	3,100	1.8
Major paraffin hydrocarbon	C_{15} 79.4%	C_{18} 12.9%
n-C_{16} ratio	4,600	8.8
CPI_{14-20}	315	0.9
CPI_{20-36}	1.7	1.0
Unresolved peak envelope C_{17} peak/C_{17-18} tangent	35.8	1.8

Recovery of Added Hydrocarbons

The addition of n-paraffins to wet mussel tissue prior to extraction was used to determine the recovery of hydrocarbons by our techniques. The lowest concentration of n-paraffins added was twice the average biogenic level found in uncontaminated mussels [3] and the highest spike added represented a maximum likely to be present in mussels directly exposed to oil in bioassay experiments [5],[6]. The recoveries of n-paraffin from mussel tissue added at three concentration levels are plotted in figure 4 and summarized in table 2. These values reflect the recovery of pure n-paraffin hydrocarbons added to the wet tissue and do not directly establish extraction efficiency of intracellular hydrocarbons.

Table II. Recovery of n-paraffin hydrocarbons from mussel tissue (*Mytilus edulis*) added at three concentration levels.

	Level I	Level II	Level III	Spiked Solvent Blank
Mean added conc. C_{14-36} a/	0.357 µg/g	1.80 µg/g	8.31 µg/g	0.962 µg b/
Recovery (%) c/ Mean ± Std. Dev.	69.4 ± 18.2	84.9 ± 10.7	95.7 ± 17.5	81.7
Mean added conc. C_{16-36}	0.358 µg/g	1.81 µg/g	8.40 µg/g	0.972 µg
Recovery (%) Mean ± Std. Dev.	92.6 ± 20.9	92.6 ± 9.6	99.9 ± 17.2	86.2

a/ Normal paraffins: 14, 15, 16, 18, 20, 22, 24, 28, 32, and 36; three replicate mussel samples (4-6 individuals) analyzed at each concentration level. Concentrations in dry extracted weight, corrected for solvent blanks; to obtain wet weight equivalents, divide by 20.9.

b/ Single determination.

c/ Recoveries expressed as mean percentage of the total of the n-paraffin hydrocarbons added to the sample ± the standard deviation.

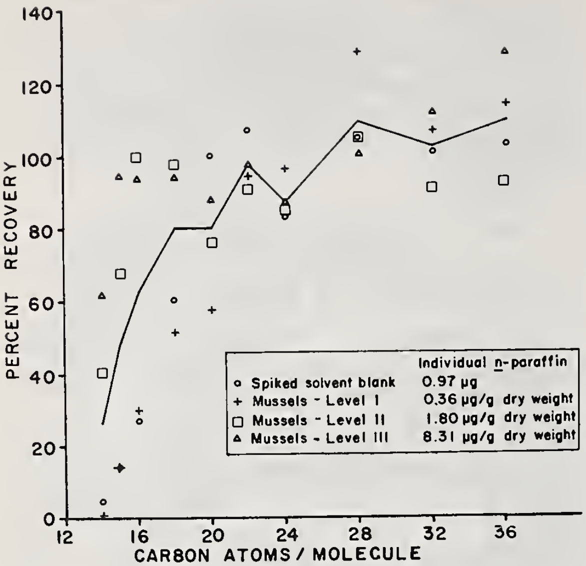

Figure 4. Recovery of added n-paraffin hydrocarbons from mussel tissue at three concentrations and from a spiked solvent blank.

On the basis of the evaluation of replicate analyses of the same species of marine organisms collected at the same location, at different locations, and at different seasons, data indicate that the reproducibility between identical samples should exceed 75%. Reproducibility as indicated by percent standard deviation (100% x Std. Dev./mean) for the sum of all n-paraffins (n-C_{14-37}) in the triplicate analyses of unspiked mussels plus the three levels of added standard hydrocarbons was 12.7%, 7.9%, 13.7%, and 9.2%, respectively.

Summary and Conclusions:

Scientists studying petroleum pollution must keep in mind that while normal paraffin hydrocarbons can be detected using the above chemical procedures, analysis of paraffin hydrocarbons in organisms may not always be the best method for detecting petroleum pollution in the aquatic environment. In cases where the petroleum pollutant is low in paraffin hydrocarbons (for example, some lubricating oils and even some crude oils), other methods must be used. Under environmental equilibrium conditions, low-level persistent petroleum pollution may be difficult to detect when the rate of biological degradation of n-paraffin is equivalent to the rate of pollutant input. Further, more research is necessary to define the limits of variability of n-paraffin analyses in aquatic populations.

Marine organisms can be used as indicators of petroleum pollution when it is possible to separate the biogenic paraffin hydrocarbons from pollution hydrocarbons. Once these paraffin hydrocarbon methods suggest petroleum contamination of a marine population, then other methods can be applied to delineate aromatic hydrocarbons to establish the extent of the pollution in the marine environment.

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Key Words: Contamination; Gas chromatography; Marine organisms; n-C_{16} ratio; Paraffin hydrocarbon; Petroleum pollution; Tissue analysis.

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DETERMINATION OF HYDROCARBONS IN MARINE ORGANISMS AND SEDIMENTS BY THIN LAYER CHROMATOGRAPHY

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The San Francisco Bay estuarine system is subject to multiple inputs of petroleum derived hydrocarbon from numerous different activities of man in the Bay area. In addition to chronic inflows which amounted to approximately 0.4 tons per day in 1969 [1], varying quantities of oil enter the ecosystem through irregular accidental spillage. Rather than attempting detailed assays concerning specific identification of hydrocarbons in the Bay, we have undertaken to analyze the "total hydrocarbon burden" in organisms and sediments as potential systems indicators of pollutant hydrocarbon levels.

Recent comparisons of hydrocarbon analyses of organisms and sediments collected at various distances from an urban source of pollution have shown a relative increase in the presence of hydrocarbons [2] [3] with increasing proximity to the source. This type of measurement is particularly promising for assays of long-term trends related to urban growth and effectiveness of oil pollution control measures where relative broad scale measurements are acceptable for monitoring purposes.

Current research at our laboratory investigates hydrocarbons in organisms as an integrative indicator of hydrocarbon insult in Bay water. Surface sediments (0-6 cm) have been analyzed as a transient hydrocarbon storage compartment with a longer residence time than characteristic of the organisms.

Thin-layer chromatography was the method of choice for reasons of simplicity, economy in instrumentation, and broad applicability in analyses of different sample types. Previous use of thin-layer chromatography (TLC) has been made to check column chromatographic eluates for the presence of contaminant lipids prior to gravimetric determination of hydrocarbons in the eluates [2]. We have employed a TLC method with simplified preparative steps in an effort to obtain a rapid qualitative and semi-quantitative assay of hydrocarbons. This methodology has been developed in order to make broad surveys of organisms and sediments where limited facilities may be available in field laboratories, and where a simplified standard method is needed for making worldwide comparisons. Samples collected at selected stations in San Francisco Bay were analyzed and compared with results obtained using the same or closely related organism species or sediment samples, collected in manifestly unpolluted waters of the northern California coast. Transfer experiments were carried out in which unpolluted mussels were placed in Bay waters, and Bay mussels in unpolluted waters, with changes in hydrocarbon burden monitored as a test of the methods.

A summary of the methodology is presented in figure 1. Tissues or sediments are extracted using a mortar and pestle with an equal weight of 550 C ashed magnesium sulfate and an equal volume of similarly ashed grinding sand. The tissue or sediment is thoroughly ground and repeatedly extracted (with grinding) using 6-10 changes of glass-distilled hexane. These procedures allow extraction of 30-50 g tissue or sediment with 300-500 ml hexane. A comparison between this method of extraction and use of the Soxhlet apparatus on the same sample showed no difference between these methods of extraction in the final TLC result. Adoption of these steps allowed for the extraction of large numbers of samples with minimal glassware requirements and low risk of contamination. The extract was then passed through a 30 x 150 mm column packed with activated silica gel, and eluted with 1.5 bed volumes of glass-distilled hexane. The extract was then concentrated to 1 ml under vacuum. TLC plates ("Uni-plates", Analtech Co., Canoga Park, Ca.) coated with Silica Gel G and containing no organic binders were pre-developed with chloroform or acetone, then air-dried. The plates were spotted with 1-10 µl sample and developed using hexane.

The plates were first observed under UV light to visualize fluorescent aromatic compounds. They were then sprayed with H_2SO_4 containing 0.25% $K_2Cr_2O_7$ and heated to *ca.* 100 C for 1 hr and 200 C for 2 hr to char the hydrocarbon spots on the plate. Hydrocarbons appeared in two groups on the plate with aliphatic compounds migrating to the upper part of the plate (R_f = 0.70-0.86) and aromatic compounds retained at the lower end (R_f = 0.05 - 0.70). Fluorescent polynuclear aromatics were observed with R_f values of 0.18 and 0.26, similar to the results of Farrington and Quinn [3]. Small amounts of polar compounds which eluted from the cleanup column were retained at the origin.

Samples from polluted and unpolluted waters were qualitatively compared for presence of aliphatic, aromatic, and

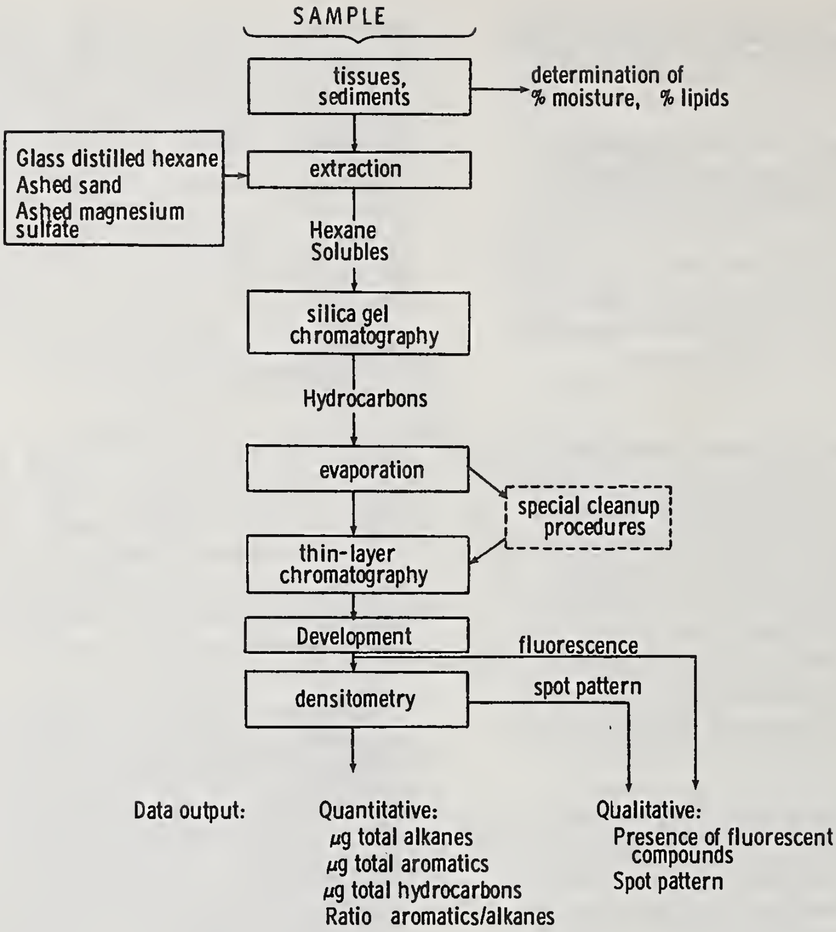

Figure 1. Flow chart of methodology.

fluorescent aromatic compounds on TLC plates as shown by figure 2. Semi-quantitative data were obtained by densitometric scanning of plates and recording of scans using a logarithmic recorder [4]. Sample values were determined from standard curves obtained with known amounts of docosane and anthracene. Determination of the charring characteristics of individual compounds indicated for normal saturated hydrocarbons about a 20% variation in spot density as a function of chain length in the 5-80 µg range. The variation observed with aromatic compounds was larger, being within a factor of 4 in the 5-20 µg range. Analysis of a mixture of saturated hydrocarbons was completed with an average relative error of 17%. The charring characteristics of a Louisiana crude oil, a Kuwait crude oil, a #2 fuel oil, a bunker fuel, and a diesel fuel oil indicated that analysis of these oils relative to anthracene was accurate to within a factor of 2.

Using present methodology, the results for complex mixtures are probably accurate within a factor of 2, as determined by gravimetric analysis of a mussel tissue sample. Three replications of the analysis of five mussel samples from the same station in the Bay showed technical and sampling variation to be non-significant at the P = 0.05 level, based on two-way analysis of variance.

Figure 3 summarizes a number of representative values obtained in analyses of organisms by the above methods. Included in the figure are comparative values obtained by other workers [2] [5] using different methods, which suggest our results to be at least valid as order of magnitude estimates. Proof of the usefulness of the method was obtained during studies of the dynamic balance of hydrocarbons in organisms transferred from polluted water to clean water and clean water to polluted water. Table I lists

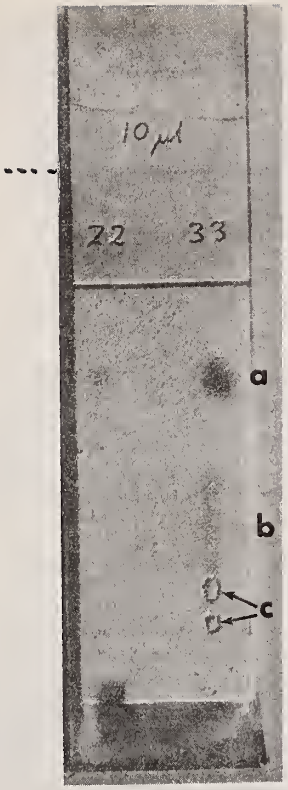

Figure 2. An example of a thin layer chromatography plate (width 5 cm) comparing hydrocarbon profiles of Mytilus samples from San Francisco Bay (33) and from the northern California coast (22). The Bay sample contains an unusually large burden of hydrocarbons in the alkane region of the plate (a), a streak of aromatic compounds (b), and two regions which showed the presence of fluorescent aromatic compounds as visualized under UV light (c).

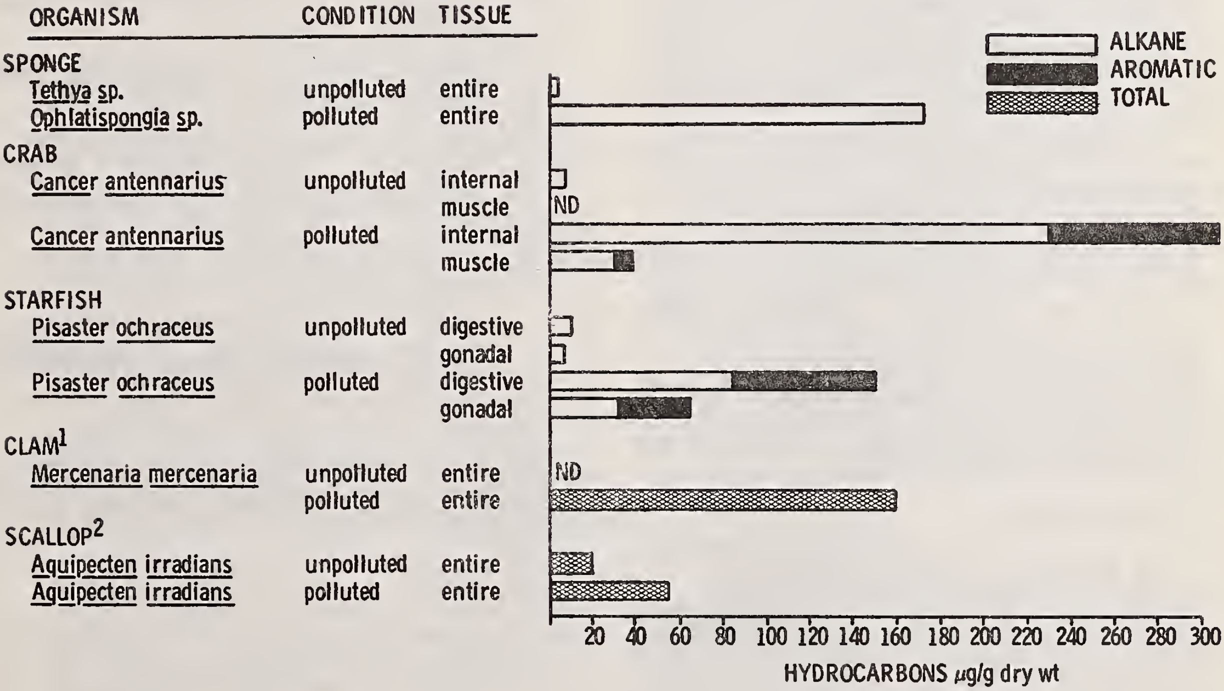

Figure 3. Comparative hydrocarbon burdens of selected organisms as determined by the TLC method. ND = not detected.

Table I. Summarized results of hydrocarbon analyses of mussels using the TLC method and transferral of organisms.

Sample	Weeks Post-transfer	Alkane	Aromatic	FPNA
		µg/g dry wt		
bkg,u	-	9 (3)	nd	−
bkg,p	-	130 (9)	154 (9)	+
u→ p	11	230	40	+
p→ u	6	25	10	±
u→ p	9	250	275	+
p→ u	6	108	75	+
u→ p	4	169	248	+

( ) = no. of samples
FPNA = fluorescent polynuclear aromatic compounds
bkg = background

p = polluted water, SFO Bay
u = unpolluted water, Calif. coast
nd = not detectable

summarized values from several transfer experiments carried out during 1973.

The method described has also been applied to sediments. In most cases the silica gel cleanup step can be omitted due to the relative absence of lipids in the sediments. Results of sediment analyses indicate that the thin layer method gave results somewhat lower than published standard methods for total hydrocarbons [6]. Known amounts of Kuwait crude oil in a sediment matrix have been determined with an average relative error of 25%.

With further standardization, this method appears to be of promise for hydrocarbon monitoring in the 1-1000 ppm (dry wt) range, where littoral or nearshore organisms or sediments are sampled. Mytilus edulis (edible mussel) is a cosmopolitan species which may be of interest in worldwide programs. Laboratory-reared mussels or other test species known to be free of petroleum hydrocarbons could be experimentally placed at any selected sampling site as integrative monitors of chronic, intermittent, low-level hydrocarbon pollution where water sampling and analysis are impractical.

Acknowledgements

We gratefully acknowledge support of the Office of Naval Research through contract to the University of California #N00014-69-A-0200-1001, as well as technical assistance provided by Ms. B. Vince.

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Keywords: Hydrocarbon profile; tissue hydrocarbons; sediment hydrocarbons, hydrocarbon monitors; San Francisco Bay hydrocarbons.

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DETERMINATION OF EXTRACTABLE ORGANIC MATERIAL AND ANALYSIS OF HYDROCARBON TYPES IN LAKE AND COASTAL SEDIMENTS

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Marine and freshwater sediments can provide a wealth of information relating to the ecological impact of industrial and domestic development. In contrast to samples of water and biota, the sediments can be considered to be reflective of local environmental conditions over a finite period of time.

A number of analytical methods have been published which provide qualitative, semiquantitative and quantitative estimates of sediment organic components. Clark and Blumer [1] reported a method utilizing solvent extraction, column cleanup and analysis of n-alkanes by gas chromatography. Mark and Yu [2] reported data obtained by direct infrared analysis of sediments. These methods are useful for rapid screening of sediment organic fractions but do not provide sufficient fractionation of organic extracts necessary for more detailed characterization of compound types.

Koons and Monaghan [3] reported a method for extraction and gravimetric analyses of organic materials in drill core samples. The method involved fractionation of total extractable organics into asphaltene and asphaltene-free organic extracts which were further subdivided by liquid chromatography into saturates, aromatics and polar compounds. This method has been adapted in the present studies for fractionation of marine and freshwater sediments. The saturate and aromatic fractions were further characterized as to compound type by application of high-voltage, mass-spectrometric techniques.

Sediment Extraction Procedure

Sediment cores, frozen immediately upon sampling, were divided into vertical segments and the surface (0-5 cm) segment were freeze-dried for a minimum of 24 hours. This procedure served to reduce the potential for biodegradation of hydrocarbons in the sediment prior to analysis.

The dried sediment (10-50 g) was placed in a pyrex thimble with a coarse, fritted-glass filter and Soxhlet extracted with 500 ml of a constant boiling mixture of benzene and methanol for 16 hours. Extraction for longer periods did not significantly increase the quantity of material extracted.

The organic extract was evaporated to dryness under a stream of nitrogen at 60°C, redissolved in benzene and filtered through a glass-wool plug to remove salts. The filtrate was evaporated to dryness at room temperature and the dry-weight determined. This material was designated as the total organic extract.

Fractionation of Sediment Extract

The total organic extract was treated with 25 ml pentane for one hour to precipitate the asphaltenes. The solution, containing pentane-soluble material, was transferred to a 80 x 1 cm column packed with 15 to 20 cm of Fisher Hyflo Super-Cel prewashed with pentane. The column was eluted with 40 ml pentane and the eluate transferred to a beaker. The eluate was concentrated by evaporation at room temperature to approximately 5 ml, transferred to a tared aluminum weighing pan, evaporated to dryness, and the dry weight determined. This material was taken as the deasphaltened extract.

The residue remaining in the beaker after removal of pentane solubles was dissolved in 10 ml benzene, transferred to the column, and eluted with an additional 30 ml benzene. The eluate was concentrated at 60°C to approximately 5 ml, transferred to a tared aluminum weighing pan, evaporated to dryness and the soluble material, designated as benzene-soluble asphaltenes, was determined gravimetrically.

The asphaltene-free extract, dissolved in 10 ml pentane, was transferred to another 30 x 1 cm column packed with 10 g Davison Grade 923 silica gel activated at 150°C for 16 hours under 10 g Alcoa F-20 alumina activated at 400°C for 16 hours. The column was eluted with a total of 70 ml of pentane. The total eluate was concentrated, dried, and the concentration of soluble material determined gravimetrically as previously described for the pentane extract. This material was designated as the saturate fraction.

The column containing the residual asphaltene-free extract was eluted with 100 ml of benzene and the concentration of soluble material in the eluate determined as previously described for the benzene extract. This material was taken as the aromatic fraction.

The column containing the remaining asphaltene-free extract was finally eluted with 100 ml of a 1:1 solution of methanol and benzene. The material in this fraction taken to contain nitrogen, sulfur, and oxygen compounds (NSO fraction) was determined as described for the aromatic fraction.

Procedural Validation

The effectiveness of the procedure employed for extraction and fractionation of petroleum hydrocarbons from sediments was validated through recovery experiments. For these studies, a known quantity of crude oil was added to the sediment in the extraction thimble prior to freeze-drying. Recoveries were determined by comparison with the results obtained from analyses of oil added directly to the solvent extraction mixture (Table I). The minimum level (350 µg/g) was

Table I. Recovery of Prudhoe Bay Crude Oil from Intertidal Beach Sediment from Puget Sound[a]

	350 µg/g	675 µg/g	1340 µg/g
ASPHALTENE FREE EXTRACT	93.3 ± 2.2	107.8 ± 2.1	94.3 ± 2.4
BENZENE SOLUBLE ASPHALTENES	106.7 ± 28.2	126.2 ± 29.5	76.3 ± 7.3
SATURATES	86.1 ± 2.9	110.5 ± 1.7	93.2 ± 2.8
AROMATICS	121.9 ± 3.3	102.0 ± 1.3	104.2 ± 1.3
NSO FRACTION	94.0 ± 4.8	94.4 ± 2.9	99.9 ± 4.4

[a] MEAN OF 3 REPLICATE ANALYSES ± STANDARD ERROR; BASED ON RESULTS OF SEDIMENT-FREE OIL FRACTIONATION

selected from a knowledge of the background hydrocarbon level in the sediment and the sensitivity of the procedure.

Recoveries ranged from 86 to 122% with a combined error from background and analytical losses not exceeding 5% at the low concentration level except in the case of the benzene soluble asphaltenes. The high recoveries and large standard errors reported for the benzene soluble asphaltenes is attributed to photosynthetic pigments and other polar material occurring as background in the sediments used for these validation studies. In general, lower standard errors were encountered at the higher concentrations.

Characterization of Sediment Organic Fractions

The concentrations of extractable hydrocarbons in lake sediments sampled at four locations exhibiting a wide range in hydrocarbon contents are shown in Table II.

Table II. Gravimetric Analysis of Lake Sediment Extracts

	SAMPLE DESIGNATION			
	A	B	C	D
BENZENE SOLUBLE ASPHALTENES, µg/g	3472	2493	1558	1191
ASPHALTENE-FREE EXTRACT, µg/g	7530	9099	1145	2234
SATURATES (% OF AFE)	24.1	21.8	17.3	10.5
AROMATICS (% OF AFE)	30.7	31.7	28.4	34.3
POLAR FRACTION (% OF AFE)	29.6	28.9	28.9	16.7

Sediments A, B, and C were obtained from locations in the vicinity of petroleum production. Sediment D was collected from an area largely free of contamination from oil-producing operations. The percentages of saturates, aromatics, and polars (NSO) are based on the starting weight of the asphaltene-free extract. These do not add up to 100%, a reflection of losses on the separation column due to adsorption of polar material. Note that sediment D is distinctive from the other three fractions, having a lower benzene soluble asphaltene content, and a different distribution of component fractions in the asphaltene-free extract.

High voltage mass spectrometric compound-type analysis can provide detailed compositional information on milligram quantities of sediment fractions which would be difficult to obtain by other means. The matrix techniques used for characterization in these studies have long been employed by the petroleum industry for routine characterization of hydrocarbon fractions. The specific procedures used in this study were derived from the work of Brown, et al. [4] who used compound-type analysis to characterize the organic material extracted from ocean waters. The compound types determined on application of mass spectrometric techniques to the saturate and aromatic fractions of the four lake sediments described above are presented in Table III. The results indicate that the fractionation techniques resulted in good separation of aromatic and saturate hydrocarbon types, with less than 2% mono-aromatic types present in the saturate fraction. In addition, the analysis revealed higher concentrations of 2 and 3-ring saturates but lower concentrations of paraffins in the sediments (A and B) containing the highest concentrations of extractable saturates. The aromatics fractions of samples C and D were found to contain substantial quantities of amorphous sulfur, which interferes with the mass spectrometric method. The use of elemental copper for removal of sulfur from hydrocarbon fractions has been described by Blumer [5]. Application of this technique to sediment fractions prior to mass spectrometric analysis is presently underway.

The procedures employed in the present studies for fractionation and characterization of the extractable organic portion of marine and freshwater sediments were well-suited to environmental studies. The quantities of organic material required for the determinations are at

Table III. High Voltage Mass Spectrometric Analysis of Sediment Extracts

	SAMPLE DESIGNATION			
	A	B	C	D
SATURATES				
CONC. IN SEDIMENT (μg/g)	1815	1984	198	235
M.S. RING ANALYSIS (HOOD MATRIX)				
% PARAFFINS	16.5	13.0	23.1	30.8
% 1-RING	27.4	25.8	41.6	27.8
% 2-RING	30.6	26.9	19.0	22.1
% 3-RING	22.4	19.0	14.2	15.2
% 4-RING	2.1	12.5	0.0	3.4
% 5-RING	0.0	2.7	0.0	0.0
% 6-RING	0.0	0.0	0.0	0.0
% MONOAROMATICS	1.0	0.1	1.7	0.8
AROMATICS				
CONC. IN SEDIMENT (μg/g)	2311	2884	325	766
M.S. ANALYSIS (HASTINGS MATRIX)				
% BENZENES	22.1	18.9	67.0[1]	[2]
% INDANS	12.1	18.1	13.3	
% INDENES	13.2	9.2	12.9	
% NAPHTHALENES	1.9	1.0	2.2	
% ACENAPHTHENES	3.6	4.0	-	
% ACENAPHTHALENES	8.7	7.5	-	
% PHENANTHRENES	3.7	4.7	-	
% PYRENES	7.5	11.5	-	
% CHRYSENES	2.3	2.5	-	
% BENZOTHIOPHENES	14.1	7.4	4.6	
% DIBENZOTHIOPHENES	7.5	11.2	-	
% NAPHTHOBENZOTHIOPHENES	3.3	4.0	-	

[1] ABOUT 50% OF THE TOTAL ION INTENSITY DUE TO SULFUR.

[2] 99+% OF THE TOTAL ION INTENSITY DUE TO SULFUR.

the milligram levels. Thus, studies of contamination in relatively unpolluted areas and in contaminated sediments are feasible. The information derived from the application of these techniques, particularly when used in conjunction with measurements of other physical and chemical properties of sediments, should assist in determination of the relationships between the source of environmental discharges and the sediment composition and in assessment of the environmental impact of petroleum producing operations.

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Key Words: Aromatic hydrocarbons in sediments, asphaltines in sediments, hydrocarbon compound types, liquid chromatography, mass spectrometry, saturate hydrocarbons in sediments, sediment organic extracts.

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HYDROCARBONS IN BLUE MUSSELS FROM THE KIEL BIGHT

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The water of the Kiel Bight receives relatively little obvious pollution by fossil fuels. Occasional minor spills are not deemed a serious problem. On the other hand, the Baltic Sea is regarded as one of the most heavily polluted water bodies though mainly be excessive eutrophication. It was an interesting question, therefore, whether or not local shellfish contained measurable amounts of petroleum hydrocarbons.

Experimental

Blue Mussels (Mytilus edulis) were used as test organisms in this investigation. Selected animals with shells approximately 7 cm long were collected by Scuba divers in April 1973 after and in January 1974 before the spring phytoplankton bloom. The mussels were sampled from a depth of 4 - 5 m (13 - 16 ft.) at a location east of the entrance to the Kiel Fjord. The place is a recreation area devoid of any industry. The animals were returned alive within a few hours after sampling and were deep-frozen immediately after arrival at the laboratory. Work-up began less than two weeks after collection of the mussels. The animals are weighed and freeze-dried without their shells. The method has been compared experimentally with the procedure described earlier (Blumer et al., 1970; Ehrhardt, 1972; Youngblood et al., 1970). Results are the same both in terms of weight and of the chemical nature of hydrocarbons extracted from the mussels.

Freeze-dried mussel tissue is extracted in purified Soxhlet thimbles for 24 hrs with n-pentane and for an additional 12 hrs with n-pentane + 25 percent benzene.

Column Chromatography

A column 30 mm wide is filled under n-pentane with approximately 100 g of deactivated silicagel (5 percent H_2O) with a bed of deactivated alumina (appro. 3 cm, 6 percent H_2O) on top. The column is washed with at least one column volume of n-pentane. The first fraction of hydrocarbons is eluted with appro. 400 ml of n-pentane. The first fraction is ended immediately prior to the appearance of a yellow band of carotinoids in the eluate. The second fraction is eluted with 200 ml of n-pentane. Fraction No. 3 is eluted with 200 ml of n-pentane + 10 percent benzene. For a detailed analysis, fractions No. 2 + 3 (column chromatography) have been separated on an activated silicagel TLC-plate. Increasing percentages of benzene in the n-pentane and finally pure methanol elute polar fractions from the column which contain the saponifiable lipids. IR- and UV-spectra are recorded of each fraction. Each fraction or an aliquot is weighed on the micro-balance.

Thin Layer Chromatography

Solvent: redistilled isooctane. TLC plate: Kieselgel 60 F 254, Merck, 20 x 20 cm. After an initial purification run the plate is activated at 220°C for 30 minutes. Immediately after cooling the mixture of substances is applied dissolved in n-pentane. The separated substances are visualized under UV-light.

Gas Chromatography

Gas chromatographic separations without subsequent mass spectral analyses were carried out on a Varian Model 2740 gas chromatograph with FID connceted with a Varian A 25 strip chart recorder. The column was 2 m x 1/16" i.d. stainless steel packed with 3 percent Apiezon L on Chromosorb W-HP, 80-100 mesh. The carrier gas was Helium. GC operating conditions were the following: The injector temperature was 200 - 210°C. The column temperature was programmed from 80 - 290°C at 6°/min. Samples are dissolved in redistilled carbon disulfide.

Mass Spectrometry

For GC-MS analyses the same gas chromatograph was operated under identical conditions except for the column packing and the carrier gas flow rate. The column was 2 m x 1/16" i.d. packed with 2 percent OV 101 on chromosorb W-HP, 80-100 mesh. The Helium flow rate was 10.3 ml/min. The mass spectrometer was an Atlas Varian CH-7 with two stage Biemann-Watson separator and differential pump system. Mass spectra were obtained under the following conditions:

electron energy: 70 eV
acceleration potential: 3000 V
beam current: 30 and 100 uA
Source temperature: 250°C
Scan: 19 linear
Amplifier: 0.1 - 1 V
Filter 3000 hz
Chart speed: 10 cm/sec

Results

The first batch of Mytilus was collected April 6, 1973. Upon freeze drying the mussel tissue lost 87.0s percent of water. The Soxhlet-extract of the dry tissue was column chromatographed. Three fractions were obtained, the latter two of which were recombined to yield fraction No. 2.

Fraction No. 1	3 mg/kg of wet tissue
	23 mg/kg of dry "
Fraction No. 2	11.7 mg/kg of wet "
	90.2 mg/kg of dry "

Gas chromatograms of fractions No. 1 and 2 are shown in Figure 1. N-heptadecane (n-C_{17}), commonly found in many phytoplankton species (Clark and Blumer, 1967) in benthic algae (Youngblood et al., 1971 loc. cit.) and in mineral oil, causes an intense peak in the gas chromatogram of fraction No. 1. It is one of a series of normal aliphatics beginning with n-tridecane and extending as far as n-heneicosane towards the end of the gas chromatogram. Pristane -2,6,10, 14-tetramethylpentadecane - (Pr) is visible closely neighboring the n-heptadecane peak. This branched aliphatic hydrocarbon is a common constituent of mineral oils, but is also found quite frequently in marine organisms (Avigan and Blumer, 1968). On the other hand, phytane, 2,6,10,14-tetramethylhexadecane, which produces a shoulder at the trailing edge of the n-octadecane peak (Ph and n-C_{18}) has not been found so far as a natural component of marine organisms. The minor siganls between the peaks of normal aliphatics have been identified by mass spectrometry as the traces of branched aliphatics. Mass spectrometry also reveals the presence of alkyl-substituted monoaromatics by intense signals at m/e 91,105, 119, 133, 147 etc. (1.11 in Figure 2). In combination, these findings confirm the suspicion that fraction No. 1 (Column chromatography) of the Blue Mussels collected in April 1973 is composed mainly of petroleum hydrocarbons with a contribution of recent biogenic hydrocarbons (e.g. n-heptadecane).

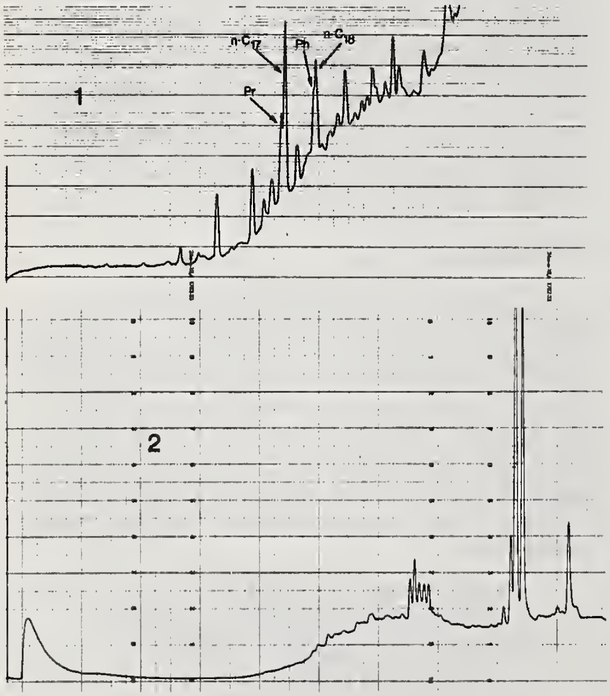

Fig.1: Gas chromatograms of column chromatographic fractions No.1 and 2 of Mytilus sampled in April 1973.

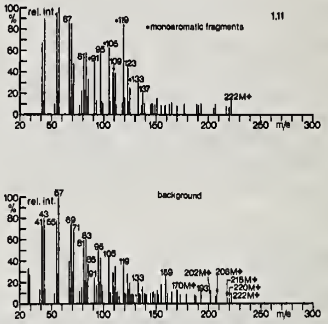

Fig.2: Mass spectra of the unresolved background of column chromatographic fractions No.1 and 2 of Mytilus samples in April 1973.

The gas chromatogram of fraction No. 2 (lower of Fig. 1) appears quite different. A number of very intense signals raise over a moderately elevated background. Mass spectra indicate C_{21}-C_{24} mono-, di-, tri-, and tetraenes.

The background of fraction No. 2 is composed of cycloaliphatics, alkylated benzenes, tetralenes, and naphthalenes. A characteristic spectrum taken from the background is shown in Fig. 2.

The second batch of Blue Mussels collected in January 1974 at the same location has been analyzed in more detail. Upon freeze-drying the animal tissue lost 91.8 percent of water. Column chromatography of the Soxhlet-extract resulted in 7 fractions whose IR-spectra are depicted in Fig. 3. From the IR-spectra it is evident that fraction No. 1 and 2 consist entirely of hydrocarbons. Fraction No. 3 contains traces of carbonyl compounds causing a small peak at 1740 cm^{-1}. For further analyses fractions No. 2 and 3 were recombined.

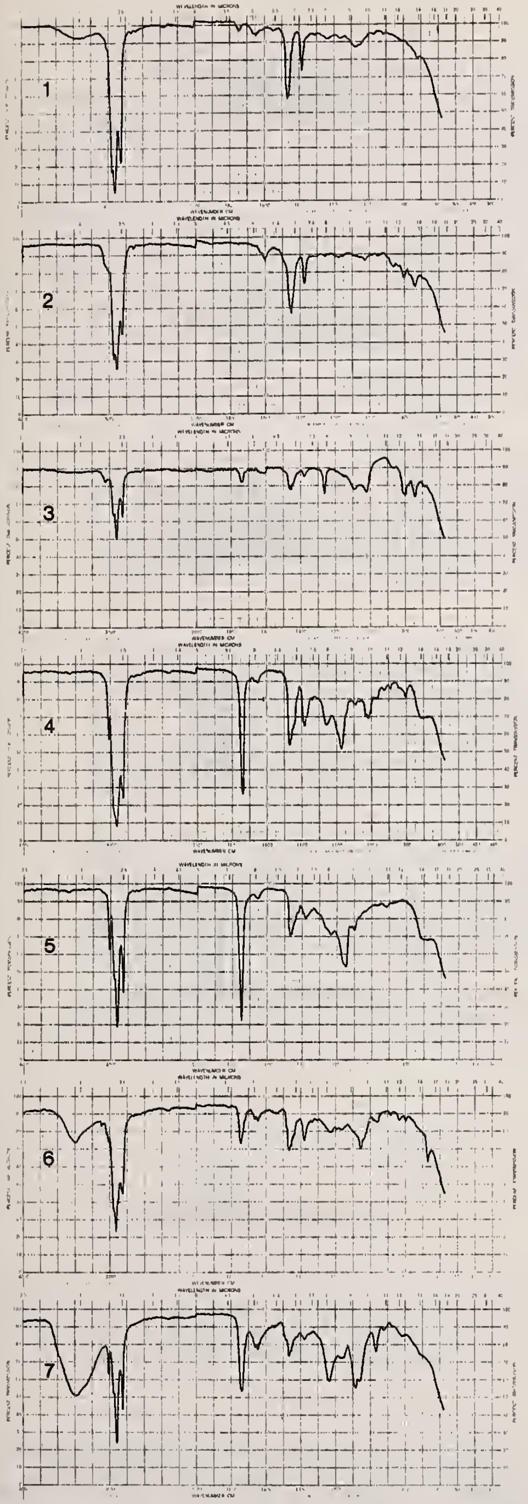

Fig.3: IR spectra of 7 column chromatographic fractions of Mytilus collected in January 1974.

Column chromatographic fractions No. 1 - 7

No.		mg/kg of wet tissue	mg/kg of dry tissue
1	6.16 mg	13.8	170
2	4.16 mg		
3	0.66 mg	10.8 (No. 2+3)	133(No.2+3)
4	29.06 mg	65.2	803
5	1397.0 mg	3135	38591
6	693.8 mg	1557	19166
7	49.9 mg	112	1278

total 2180.74 mg

recovery: 83.2 percent

TLC-fractions No. 2.1 - 2.4

No.		mg/kg of wet tissue		mg/kg of dry tissue	
2.1	1.662 mg	3.7	5.6	45.9	68.9
2.2	0.845 mg	1.8	2.8	23.3	35.1
2.3	0.297 mg	0.7	1.0	8.2	12.3
2.4	0.086 mg	0.3		3.6	

The gas chromatograms of fractions No. 1, 2.1, 2.2, and 2.3 are shown in Fig. 4. The numbered vertical bars mark the positions of mass spectra. A comparison with fraction No.1 of the batch of mussels collected in April 1973 (Fig. 1) reveals striking differences. In fraction No. 1 of the mussels collected in January 1974 the peak intensities of normal hydrocarbons are much diminished relative to the background and relative to pristane (Pr) and Phytane (Ph). The peaks of these branched aliphatics have approximately both gas chromatograms. The peak of one presumably recent biogenic hydrocarbon (fraction No.1, Fig.4) rises above all others. The mass spectrum (2.6 in Fig.5) indicates a molecular weight of 344 corresponding to the general formula $C_{25}H_{44}$.

A mass spectrum of the background positioned at 5 (2.5 in Fig.5) shows peaks characteristic of alkanes, cycloalkanes (m/e 83, 97 etc.) monoaromatics (m/e 119, 133, etc.) tetralenes (m/e 145, 159, etc.), (Ehrhardt, M., 1972,loc. cit. and references cited therein).

Some characteristic mass spectra of fractions No.2.1, 2.2 and 2.3 are shown in Fig.6. The mass spectrum 2.1.3 is characterized mainly by three fragmentation series: monoaromatics with fragments at m/e 105, 119, 133 etc., tetralenes with fragments at m/e 145, 159, 173 etc., and naphthalenes with fragments at m/e 115, 141, 155. Spectrum No. 2.1.4 is characteristic for phenylcycloparaffins.

Spectrum No.2.1.6 shows a fragmentation series produced by hydrocarbons of the general formula C_nH_{2n-14}, among them alkylated biphenyls, and of the general formula C_nH_{2n-12} denoting alkylated naphtalenes.

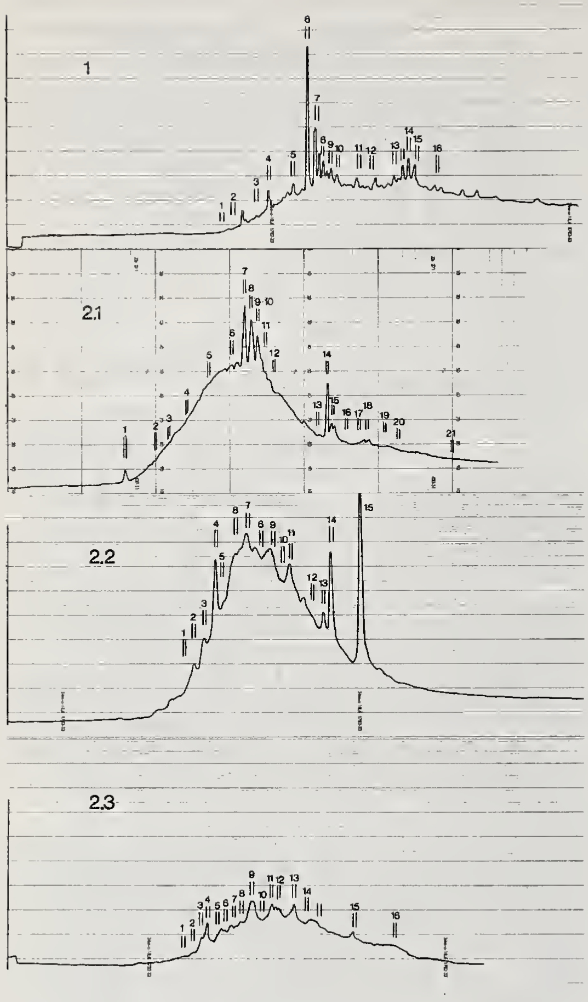

Fig.4: Gas chromatograms of 4 fractions (column chromatography and TLC) of Mytilus collected in January 1974

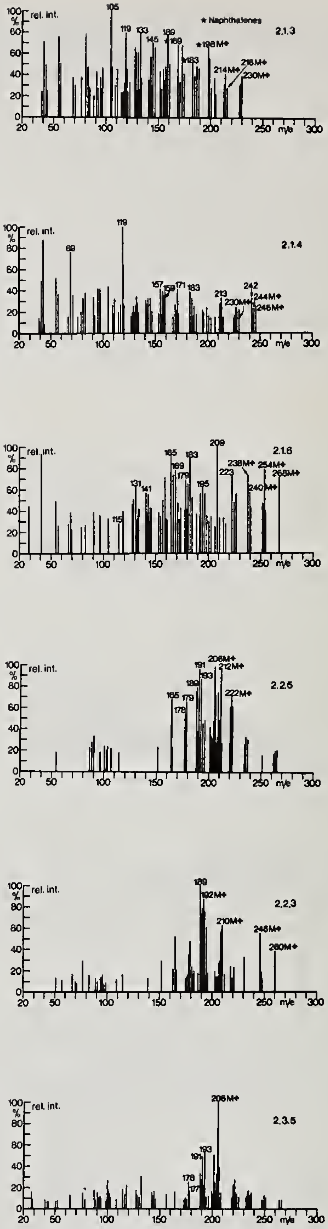

Fig.6: Characteristic mass spectra of TLC-fractions 2.1, 2.2 and 2.3 of Mytilus collected in January 1974.

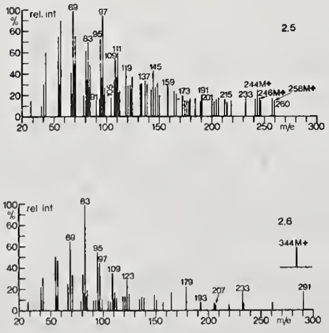

Fig.5: Mass spectra from fraction No.1 of Mytilus collected in January 1974.

Spectrum No. 2.2.5 has intense peaks at m/e 165, 179, 193 and a corresponding molecular ion peak at m/e 222. This series is in good agreement with the fragmentation pattern of alkylated flourenes. m/e 206 is the M+ -peak of a dimethylphenanthrene, and m/e 208 denotes an alkyldihydrophenanthrene. No.2.3.5 is interpreted as the mass spectrum of, primarily, a dimethylphenthrene (MG 206).

Conclusions

Blue Mussels (Mytilus edulis) from a location in the Kiel Bight, contain fossil hydrocarbons in concentrations somewhat above the natural background of recent biogenic hydrocarbons. The composition of the hydrocarbon fraction is not constant. Mussels collected after the spring phytoplankton bloom contain relatively large amounts of recent biogenic hydrocarbons whose concentrations in mussels collected in January are quite low. On the other hand, concentrations of cycloalkanes, mono-, di-, and tri-aromatics as well as mixed types of fossil origin have a tendency to rise. The experimental results may be interpreted as follows:

1) The mussels exchange hydrocarbons with the surrounding water which contains a relatively constant if not rising concentration of fossil hydrocarbons in addition to recent biogenic hydrocarbons whose concentrations vary seasonally.

2) The mussels are able to degrade recent biogenic hydrocarbons which they ingest with their food and take up from the water, but are much less efficient in degrading cyclic saturated and aromatic hydrocarbons originating from fossil fuels.

3) Some time near the start of the experiment the mussels were exposed to oil pollution. Subsequently, they exchange saturated and olefinic hydrocarbons much more rapidly with the water than cyclic and aromatic hydrocarbons.

Present data are insufficient to decide on one of the three interpretations given above or a combination thereof. As a working hypothesis it is assumed that hydrocarbons introduced as pollution and excreeted by phytoplankton are predominantly injected at or near the sea surface. Subsequently, they are adsorbed onto or dissolved in particulate matter, because the partition coefficient should favour the solution of hydrocarbons in the lipids of detritus. Detritus then carries the adsorbed or dissolved hydrocarbons to the seafloor where they are ingested by filter-feeding organisms.

Acknowledgement

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TOPICAL SESSION V.
Tar Balls and Particulate Matter: Analytical Methods

NBS Spec. Publ. 409, Marine Pollution Monitoring (Petroleum), Proceedings of a Symposium and Workshop held at NBS, Gaithersburg, Maryland, May 13-17, 1974 (Issued December 1974).

IDENTIFICATION OF MINERAL OILS BY FIELD IONIZATION MASS SPECTROMETRY*

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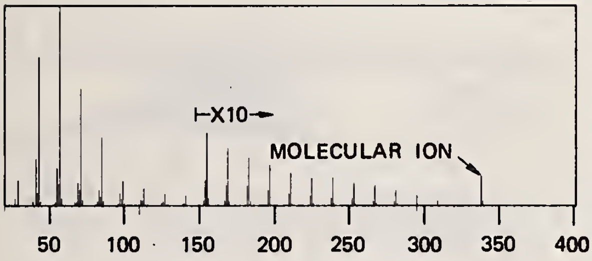
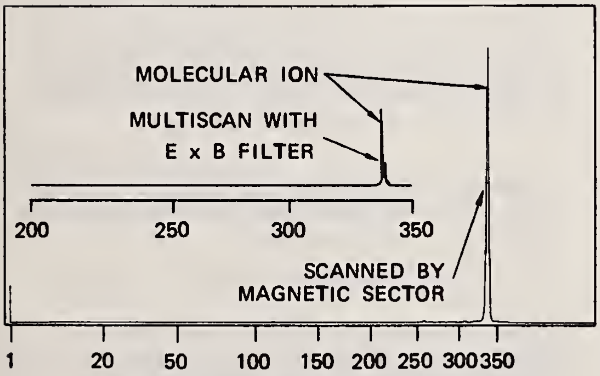
It has been reported that crude and fuel oils may be identified through their nonfragmented mass spectra using field ionization mass spectrometry [1,2]. Unlike conventional electron impact ionization (EI), field ionization (FI) of organic molecules produces virtually no ionic fragments. Figure 1 presents the mass spectra of n-tetracosane ($C_{24}H_{50}$) by EI and FI. It is evident that FI produces only the molecular ions.



(a) ELECTRON IMPACT SPECTRUM OF n-TETRACOSANE, M.W. = 338.67



(b) FIELD IONIZATION SPECTRUM OF n-TETRACOSANE, M.W. = 338.67

TA-340583-1

FIGURE 1

Figure 2 presents a mass spectrum of four pure hydrocarbons in the mass range 255 to 311. The molar fractions of the constituents may be compared with the total ion count of each molecular ion. It is evident that FI provides, in addition to unambiguous qualitative information, meaningful quantitative data.

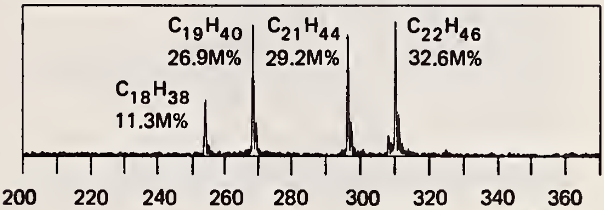


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FIGURE 2 FIELD IONIZATION MULTISCAN OF FOUR PURE HYDROCARBONS

Field ionization is facilitated by the high field gradient that can be produced at surfaces with very high curvatures. A cathode with a radius of curvature of about 0.1 μ and an anode at a distance of 75 μ require less than 3000 V to produce field ionization. Such a configuration is readily attainable in a reproducible manner by the appropriate technology. At SRI we developed the technology for producing arrays of hundreds of microcones on a porous substrate [3]. These arrays constitute the crucial element in our present ionization sources. They allow better sample feed and more uniform and reproducible operation than field ionization sources previously used. Figure 3 shows the cross section of an operational field ionization source in which the temperature of the sample can be controlled independently of the temperature of the source.

The ionization efficiency of our screen-mounted ionization sources is 5 x 10^{-4} or higher [4], and the ionization efficiencies of individual components in a mixture are independent of each other [4]. However, owing to the relatively large area of our ionization source (about 2 mm^2), the high energy of the ions produced, and their divergence, the overall efficiency of the present generation of field ionization mass spectrometers is only about 10^{-8} for instruments with a magnetic sector or a Wien ion velocity filter, when these mass analyzers reach resolutions of 800-1000. In the analysis of crude and fuel oils, where we are not sample limited, this sensitivity is completely adequate. Thus 100 μg of material, which is an adequate sample, allows us to determine with a 3% precision even components that constitute 10^{-4} of the total mixture (when we scan over a range of 200 amu).

Thanks to its nonfragmenting nature, FI allows the analysis of multicomponent mixtures. Each peak in a mass spectrum of such a mixture is a measure of the abundance of a single constitu-

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* This work is sponsored by the U.S. Coast Guard under Contract DOT-CG-22996-A.

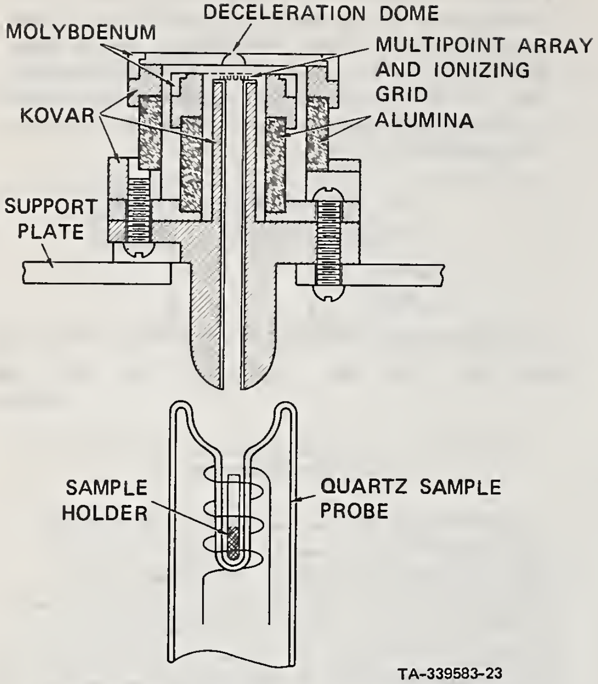

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FIGURE 3 SCHEMATIC CROSS SECTION OF MULTIPOINT IONIZER SHOWING DECELERATION LENS AND SOLID SAMPLE PROBE

ent or of the sum of all the isomers and isobars having the same gross molecular weight. It should be remembered that the composition of the vapor phase over a multicomponent mixture changes as it evaporates into the ionization source, leaving the less volatile constituents behind. To achieve reproducible quantitative analysis of multicomponent mixtures, one can integrate many rapidly scanned mass spectra of the mixture, obtained while it evaporates through the ionizing grid, into a composite mass spectrum that represents quantitatively the composition of the sample. The requirements in this case are that the change in composition of the vapor phase during each individual scan be minimal and that the scanning be continued until complete exhaustion of the sample.

We have adapted the E x B Colutron ion velocity filter for a multiscanning mode of operation. Figure 4 is a schematic description of the instrument. The ramp voltage taken from the time base of the multiscaler is amplified after conversion to a linear mass-time dependence to produce a changing voltage on the electrostatic plates of the velocity filter. Figure 5 is a multiscan of a crude oil sample produced on this instrument. The resolution of 800 obtained here is an important achievement considering that this is a composite spectrogram obtained from hundreds of individual scans.

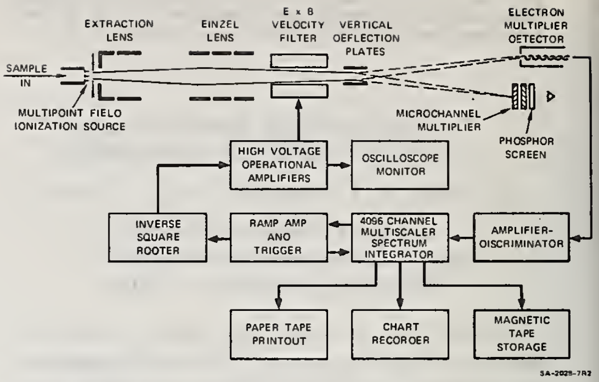
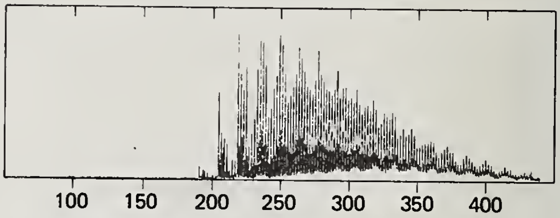
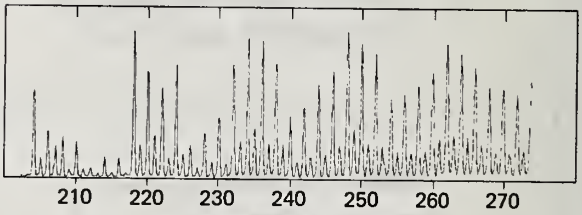


FIGURE 4 SCHEMATIC OF FIELD IONIZATION FINGERPRINT APPARATUS



(a) INTEGRATED MASS SPECTRUM OF MID-CUT QUIRIQUIRE VENEZUELA CRUDE OIL OVER WIDE MASS RANGE



(b) EXPANDED SECTION

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FIGURE 5 INTEGRATED MASS SPECTRUM OF MID-CUT QUIRIQUIRE VENEZUELA CRUDE OIL OVER WIDE MASS RANGE

Figure 6 presents highly expanded sections of multiscan fingerprint spectra of crude oil. This figure is hand-drawn from the digital data printout of the multiscan spectrum.

The application of the integrated multiscan methodology to the identification of oil slicks is shown in Figure 7. There is no difficulty whatsoever in distinguishing between each of the three No. 6 fuel oils, or each of the three crudes presented in Figure 8, and it also is easy to see the similarity between the repeated spectra of the same crude oil.

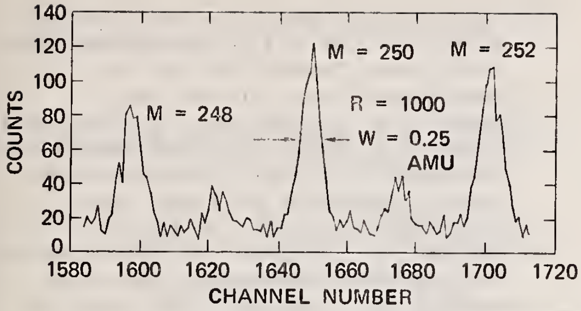

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FIGURE 6 EXPANDED PLOT OF VENEZUELAN CRUDE OIL FINGERPRINT

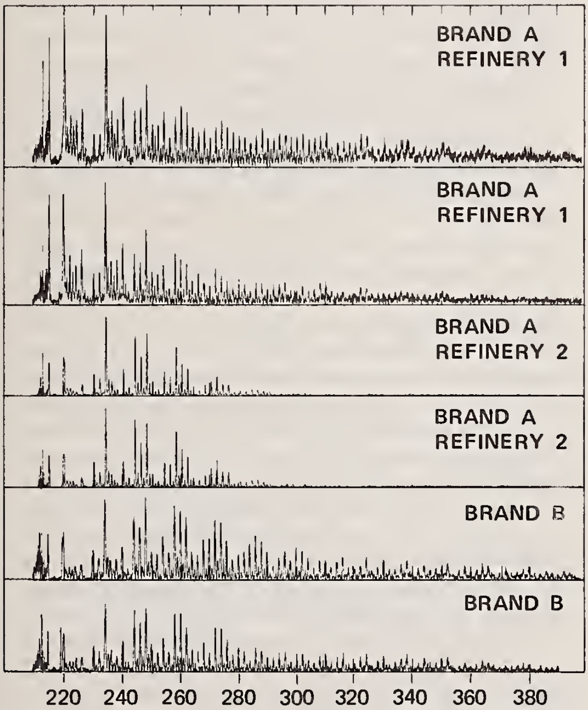

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FIGURE 7 FINGERPRINTS OF NO. 6 FUEL OILS

Figure 9a is an integrated multiscan spectrum of a front cut (up to 140°C, 50 μ) of the same fuel oil No. 6 shown in Figure 9b.

Comparing Figures 9a and 9b, it is clear why we prefer to take a mid-cut from the oil. The low molecular weight constituents may readily vary from one sample to another because of accidental evaporation, and the heavier fraction adds little information while considerably increasing the analysis time before achieving complete evaporation of the sample through the ionization source.

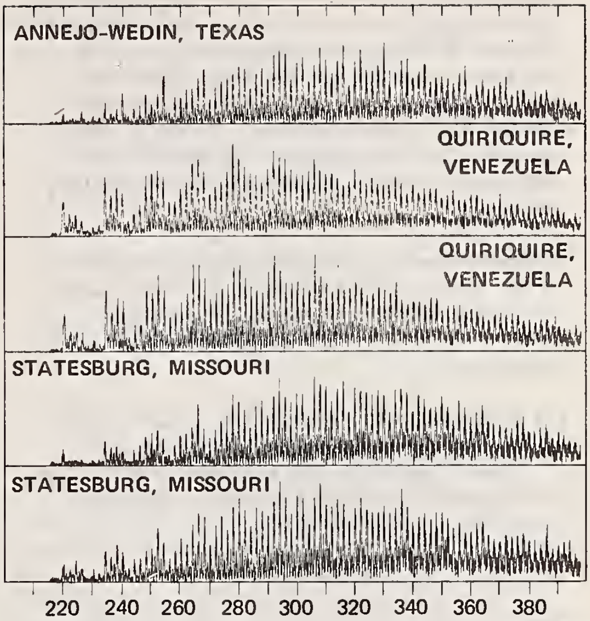

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FIGURE 8 FINGERPRINTS OF CRUDE OILS

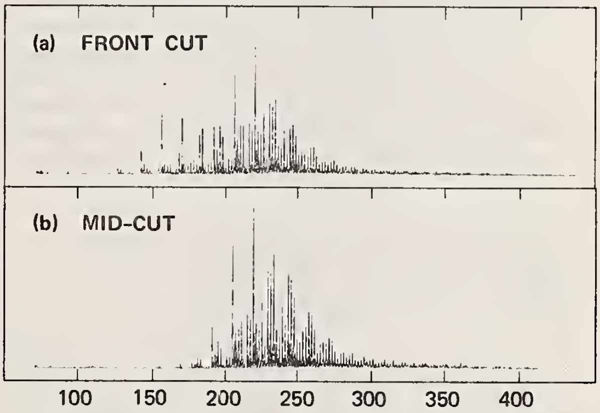

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FIGURE 9 INTEGRATED MASS SPECTRUM OF NO. 6 FUEL OIL—100°C @ 100 MICRONS AND 140°C @ 50 MICRONS

Routine identification of a sample of unknown origin by comparison with a library of mass spectra of known origin must be carried out by computer analysis. Description of this methodology, which is now under development, is outside the scope of this presentation.

In conclusion, any passive "fingerprint" method for the identification of the origin of oil spills must be evaluated by the amount of reproducible, quantitative, and characterizing information it provides about a given oil sample. The more quantitative information provided about the sample, the higher the probability of positive identification, and the lower the chances for false positives. Based on these criteria field ionization fingerprint mass spectrometry seems to surpass other competing techniques.

Acknowledgement: The authors wish to thank Dr. Alan P. Bentz of the U.S. Coast Guard R and D Center for helpful discussions.

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NBS Spec. Publ. 409, Marine Pollution Monitoring (Petroleum), Proceedings of a Symposium and Workshop held at NBS, Gaithersburg, Maryland, May 13-17, 1974 (Issued December 1974).

PELAGIC TAR IN THE GULF OF MEXICO AND CARIBBEAN SEA

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The Gulf of Mexico might be expected to have a relatively high pelagic tar concentration, because it is a semi-enclosed sea with a weak circulation in the central and western parts and because of its extensive offshore oil production and tanker traffic. Since there was inadequate information on floating tar distribution in both the Gulf of Mexico and Caribbean, 104 samples of floating tar were collected on cruises of Texas A&M University's R/V Alaminos and Gyre. Half of the samples were collected with a one-meter plankton net (mesh size 240) with floats attached to sides of the mouth of the net, so it would travel evenly in the water half submerged. The other half of the samples was collected with a semi-quantitative neuston net, which was 2 m wide and 10 m long with a mesh aperture of 1 mm. When attached to a 1 × 2 m tubular aluminum frame and towed at 2 knots, the net fished evenly to a depth of 0.5 m. The nets were towed for 30 to 60 minutes at an average speed of 2 knots. Area of sea surface skimmed was 18,500 to 37,000 square meters. The net contents were transferred as quantitatively as possible to glass jars and frozen. In the shore laboratory, the tar was hand-picked from the samples, dried and weighed. Tars were then dissolved in benzene and the solution filtered through Gelman Type A fiberglass filters to remove the debris. The filtered solution was then evaporated to constant weight in a circulating air oven at 50°C. The concentrations of pelagic tar expressed as mg tar/m^2 were calculated from the benzene-soluble dry weight and the area towed.

The locations of the tar stations and the approximate concentrations are shown in Figure 1. Pelagic tar concentrations in the Gulf of Mexico ranged from 0 to 10 mg/m^2 with an arithmetic mean concentration of 1.20 mg/m^2. In the Caribbean, the pelagic tar concentration ranged from 0 to 4.51 mg/m^2 with an arithmetic mean of 0.74 mg/m^2. There were 84 samples for the Gulf of Mexico and 20 for the Caribbean.

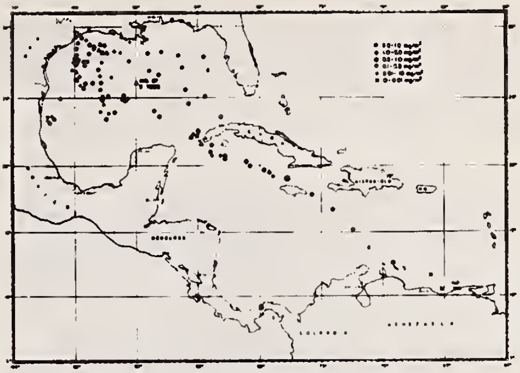

Figure 1

From the available data, it appears that the Gulf of Mexico as a whole has lower concentrations of pelagic tar than the Mediterranean Sea and the Sargasso Sea and the Northwest Pacific (See Table I). The Gulf of Mexico appears to have slightly more tar than the Caribbean, and the Northwest Atlantic marginal sea and probably about the same concentration as the Gulf Stream. It should be pointed out that pelagic tar concentrations reported in the literature by Wong, et al. [1], Butler, et al. [2] and Horn, et al. [3] were obtained from wet weights and are not strictly comparable to the data reported here. Our results show that the non-tar particulates amounted to an average of 36.6% of the dry weight with a range of 5-77% of the dry weight. Probably, there are insufficient data in all these marine areas to warrant any final conclusions.

Table I. Comparison of Pelagic Tar Concentrations in the Gulf of Mexico and Caribbean with those of Other Marine Areas

Region	No. Samples	Range (mg/m^2)	Mean Tar Concentrations (mg/m^2)
Gulf of Mexico*	84	0-10.0	1.20
Caribbean Sea*	20	0-4.5	0.74
Northwest Pacific [1]	15	0.3-14.0	3.8
Northeast Pacific [1]	18	0.0-2.9	0.4
NW Atlantic Marginal Sea [2]	8	0.0-2.4	0.9
Gulf Stream [2]	16	0.1-9.7	2.2
Sargasso Sea [2]	34	0.1-40.0	9.4
Mediterranean [3]	41	0.0-540	20.0

* This work

In an attempt to determine the general sources of the pelagic tars, gas chromatography, asphaltene and sulfur analyses were determined for 50 pelagic tars and for comparison purposes, also on 78 beach and 13 abyssal tars dredged from the bottom of the western Gulf of Mexico.

Gas chromatography of the tars were done on a 6-foot, 3% SE-30 on Chromsorb P column in an F and M Model 700 gas chromatograph with a flame ionization detector. Temperature programming from 100° to 290° at the rate of 10°/minute was used for separation of the hydrocarbons. Total sulfur percentage was determined on the tars by combustion in a Leco furnace and iodometric titration of the SO_2 (ASTM method E30-47). Precision of ± 3% of the total sulfur was obtained. The percentage asphaltenes was determined by exposing one gram of tar at room temperature to 40 ml pentane three times for an hour each time. The material insoluble in pentane but soluble in benzene was the asphaltene fraction.

All the gas chromatograms of the pelagic tars had sharp spikes above the baseline with very little humping in contrast to many beach and abyssal tars which often had very small or no spikes and much humping. Thirty-two percent of the pelagic tars showed a bimodal distribution of peaks, which, according to Butler, et al. [2] represent tanker sludge residues. The remainder of the gas chromatograms appeared to be mostly crude oils from their carbon chain number range and distribution of hydrocarbons. No attempt was made to relate the tars to specific sources. C_{24}/C_{20} and C_{20}/C_{17} ratios were calculated when possible to determine the number of sources. It was not possible to do so with most of the beach tars and abyssal tars, because they were too weathered. The number of sources for the pelagic tars was at least 15, on the basis of gas chromatograms.

In Figure 2 it is shown that fifty percent of the pelagic tars had 1-2% sulfur, 27% had < 1% sulfur and about 10% had > 3% sulfur. In sharp contrast, all the abyssal tars had > 3% sulfur with a range of 3 to 8%. The sulfur content of the beach tars had a much broader range than the pelagic or abyssal tars. From the available data on the effect of weathering on sulfur content of oils, and on the % sulfur of crudes produced worldwide, it seems possible that at least 60% of the pelagic tars did not originate from U.S. northern Gulf Coast oils but from foreign crudes from the Caribbean or the Middle East. The 27% of pelagic tars with a sulfur content < 1% could possibly have originated from northern Gulf Coast oils. The origin of the high sulfur abyssal tars could be the remnants of oil seeps or sinking of dense, weathered, high sulfur pelagic tars. From their large size and lack of particulate material in the matrix, we tend to believe the former. The beach tars obviously had many sources, but the highest percentage contained > 2% sulfur, which again indicates perhaps a foreign high sulfur oil transported by ships and/or currents.

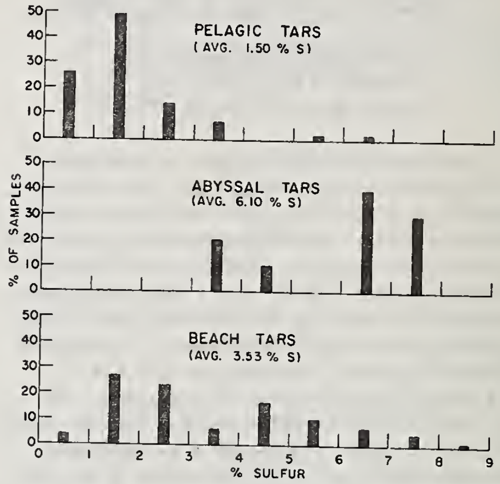

Figure 2

All the tar samples contained > 5% asphaltenes. In general, asphaltene content was highest in abyssal tars with an average of 55%; pelagic tars had an average of 26%; and beach tars an average of 32.1% as shown in Figure 3. The majority of pelagic and beach tars were in the range of 10 to 30% asphaltene.

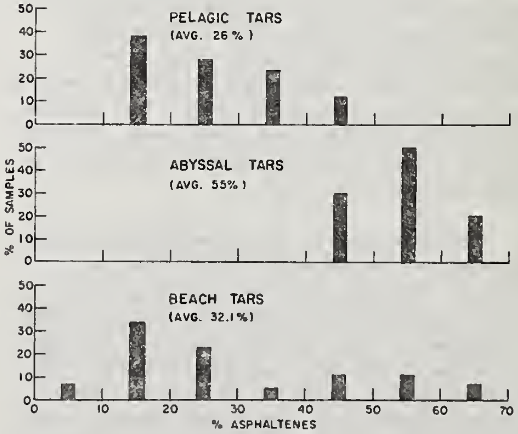

Figure 3

In general, asphaltenes are not lost during weathering processes, so these compositions are dependent on the initial asphaltene content of the oil and weathering of light compounds. A number of northern Gulf Coast oils and light fuel oils do not form tars because they contain no asphaltenes. Percentage asphaltenes on the environmental tars is not as diagnostic as we had hoped, so we are currently obtaining gel permeation chromatograms on the asphaltene fractions which appears to be more diagnostic.

In summary, the Gulf of Mexico apparently has less pelagic tar than the Mediterranean and Sargasso Sea, but more than the Caribbean and northeast Pacific and about the same amount as the Gulf Stream. Some of the pelagic tar is swept into the Gulf of Mexico through the Yucatan Straits and out through Florida Straits and primarily from shipping and tanker cleaning operations. Specific sources are difficult to ascertain on these obviously weathered materials, so a multi-parameter approach is necessary. Other diagnostic parameters recommended for study are CHN, trace element composition of the tars and the molecular size patterns of the asphaltene fraction. A catalog of such information is needed for many weathered crude and fuel oils from all over the world to pinpoint environmental "tar ball" sources.

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Key Words: Pelagic tar, Tar balls, Gulf of Mexico tar balls, Caribbean tarballs, Sulfur of tar balls, Asphaltenes of tar balls.

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MARINE ENVIRONMENTAL MONITORING: TRACE ELEMENTS IN PERSISTENT TAR BALL OIL RESIDUES

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INTRODUCTION

The quantitative characterization of oil pollution and residues in the sea has been the subject of numerous investigations. Methodology choices have been dependent on the particular goal of the investigation. Thus, the overall descrption of the oil, or at least of the non-polar hydrocarbon chemical species in it, has been perceived as the essence of the problem, and has led to elaborate testing procedures for characterization of these materials in water, sediments, and biota. See Figure 1, which shows some well known procedural approaches to the analysis of petroleum pollution of the sea, developed by Blumer (1972), Farrington (1972), and Levy (1973).

A significant new aspect of monitoring of oil pollution, a persistent fraction resulting in tar balls has been described, and a review of the information available has been presented (Butler 1973). Possible ecological importance of these materials has been discussed, in terms of Trace Material Interaction of Oils and other materials present in the surface films and slicks on marine waters (Feldman 1973a).

Analysis of tar balls by gas chromatography (Levy 1973) actually only gets at about half of the material. This is probably due to the high boiling character of some of the material (Butler 1973), (Koons (1973).

METHODS

In attempts to get a forensic system for government regulatory procedures against oil polluters some workers have utilized Instrumental Neutron Activation Analysis (INAA) as a finger printing device, (Guinn, 1970), and some have examined the weathered fraction of the petroleum for a similar purpose (Filby 1971).

Using readily procurable stock items, an automated equipment, shown in Figure 2, utilizing computer data analysis, has been developed, (Feldman 1973b).

After suitable irradiation and decay, a set of samples is placed in the counting and recording system consisting of a Nuclear Chicago, Model 1085, mechanical sample changer, which is coupled to and controlled by a Nuclear Data 2200 Pulse Height Analyzer (PHA). The PHA records signals (pulses from the 15% efficiency, 2.3% resolution, Ge(Li) crystal[*] in its 4096 channel memory through a 50 megaherz ADC. At the conclusion of a preset count period the data is read out into either:

a. A telephone line feeding directly to the computer[**], or
b. A magnetic tape bulk data storage system based on Kennedy tape transport model 3112.

Routine analysis utilizes the tape; experimental development work utilizes either the wire or the tape or both. The tape is hand carried to the computer at the end of a sequence of samples for subsequent interrogation and printout of tables of data as allowed for in our computer programs.

All of the relatively unsophisticated programs which allow diversity of application were each generated, as the need became obvious, as a convenience to allow a technician to carry out simple laboratory procedures and to have voluminous data handled for him as a substitute for rather pedestrian data printing and hand computation. The program items presently available allow for:

1. Area calculation of any "regions of interest" whose boundary channel numbers are specified to the computer. These areas are corrected for background, compared to standards similarly specified, and subjected to standard deviation statistical examination. This program is particularly useful for tracer experiments generating many samples with a few radionuclides, known to be present. It is also useful for computer interrogation where a specific nuclide is being evaluated experimentally for procedure development.

2. Calibration of the 4096 channels of the PHA for a range of energies by use of a set of standard materials (Filby 1970) or more often by the use of an element like europium-152 which has several well-known gammas over the range of energies generally

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[*] Compared to a 3" NaI crystal and using a Co-60 1.33 MeV line; by the manufacturer, EDX International, Prairie View, IL.

[**] Oregon State University (OSU), Control Data Corporation 3300 + OS3 operating system.

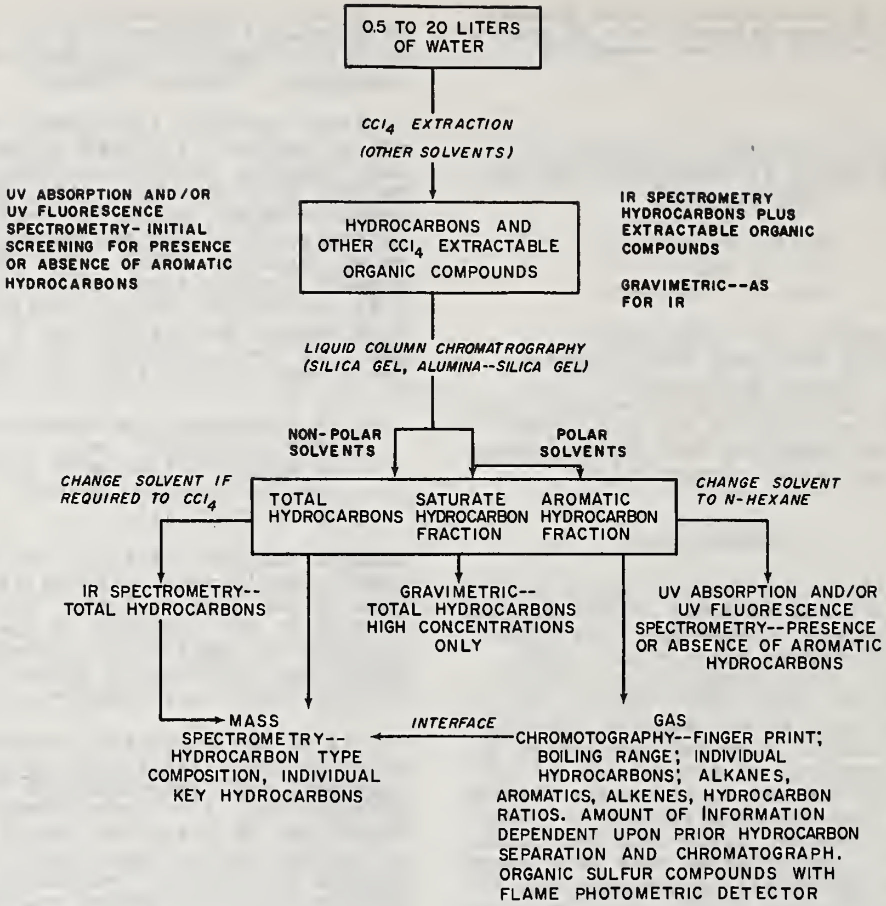


Figure 1. Flow diagram for analytical techniques to measure C_{10} plus hydrocarbons in waters (Levy 1973).

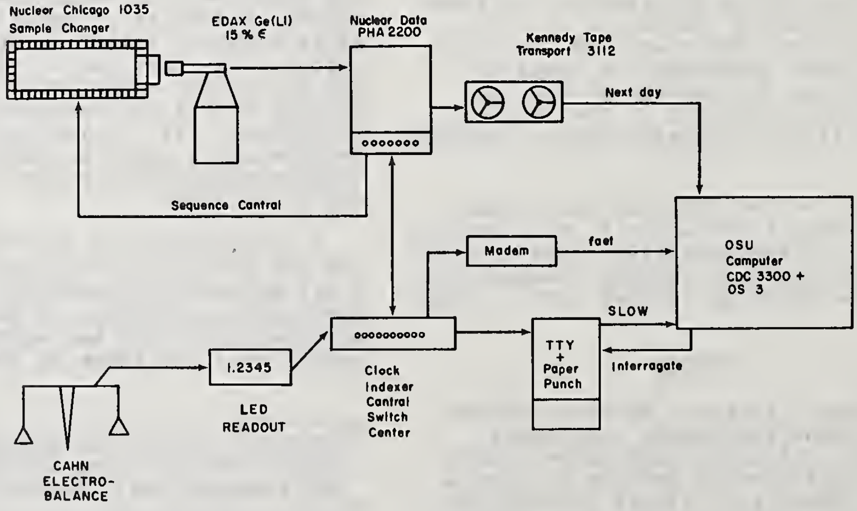


Figure 2. Schematic of automated equipment.

used. Comparison of any unknown peak is by interpolation between the closest peaks used in the calibration.

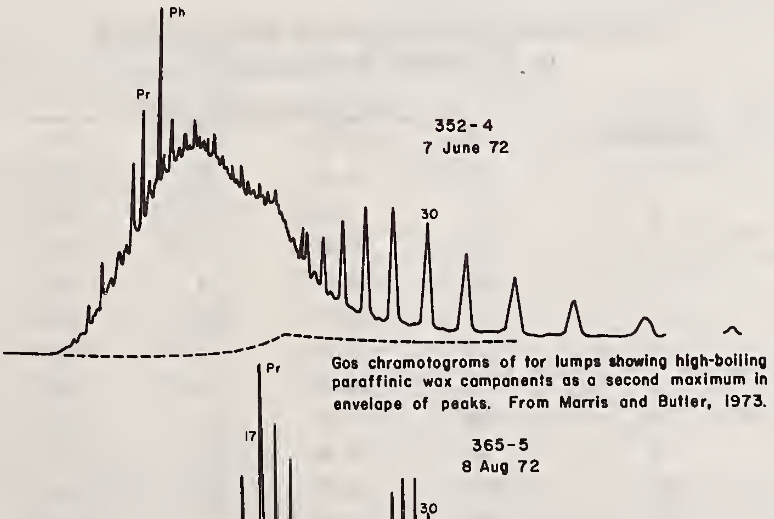
3. Peak searching by observation of changes of slope between successive sets of channels by the procedure of Feldman (1973b), locates the edges of the peak, the peak energy, estimates the area of the peak, corrects for background, and estimates the standard deviation of the area. Printout of this information comprises the essential data of the system for quantification. Program item 4 which involves a degree of judgment is of equal importance in developing reliable procedures.

4. The computer program has access to a very complete library of data on thermal neutron generated activities. Relevant data on both sides of the energy of the peak of interest over any desired energy span is easily evoked and printed out. Along with the gamma energies there is printed out: nuclides, half lives, abundances, cross sections, accompanying gammas. This information allows, in most instances, decision as to identity, as well as quantitation; in some instances additional information from decay is required. Energy and decay data generally are adequate for positive identification as well as quantitation.

5. Decay information of a given peak or set of peaks in a sequence of counts is always desirable in developing procedures for samples of a newly given set. The use of the tape for recording a set of samples' changing spectra with time by repetitive counting in the mechanical sample changer gives a set of data that can easily be used for this purpose. Thus, suppose 18 samples are counted ten times in a 48-hour period. Then the tape data in the computer are queried for a given peak (region of interest per program item 1) in repetitive spectra for a given sample or samples and the results plotted using a simple least squares statistical evaluation to obtain the decay constant for each nuclide peak of interest.

RESULTS

Figure 3 shows typical information obtained by gas chromatographic examination of tar balls. Figure 4 shows some typical information which may be obtained by means of neutron activation of tar balls. Table 1 (Guinn 1970) shows that a variety of oils may be readily monitored by neutron activation. All of the data taken in this demonstration of trace elements in tar balls are given in Table 2. Comparison to the data in Table 1 suggests that significant trace element content in tar balls should be considered for ecological impact evaluations for both oils and tar ball residues (Feldman 1973a).



Gas chromatograms of tar lumps showing high-boiling paraffinic wax components as a second maximum in envelope of peaks. From Morris and Butler, 1973.

Figure 3. Typical information obtained by gas chromatographic examination of tar balls.

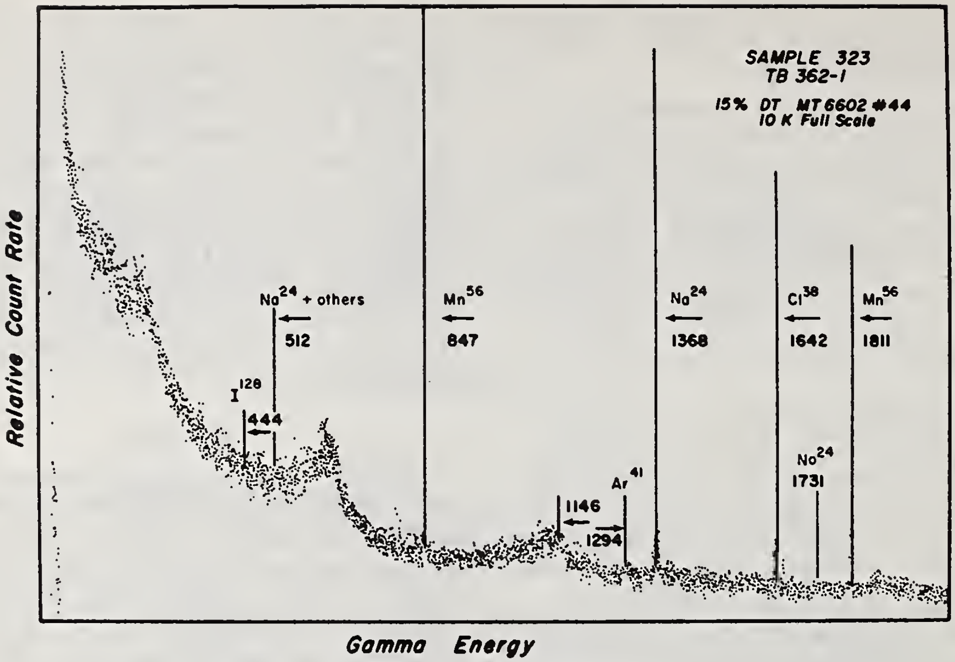


Figure 4. Typical information obtained by neutron activation of tar balls.

TABLE 1

Instrumental Neutron Activation Analysis Results on 16 Different Marine Fuel Oils

Oil Number	ppm Concentration Found			
	V	Mn	Na	Co
1	17.5	<0.30	35	0.92
2	175	0.043	7.9	0.39
3	220	0.020	1.69	0.62
4	470	0.077	44	0.41
5	77.6	<0.37	108	1.84
6	170	0.011	2.12	<0.07
7	3.8	0.002	0.36	0.08
8	865	<0.19	38	0.13
9	91	<0.39	25	0.40
10	250	<0.24	19	0.40
11	126	<0.23	7	0.23
12	284	0.08	12.4	0.25
13	292	<0.28	85	0.35
14	208	0.07	6.3	0.21
15	152	0.24	32	0.57
16	57.5	0.113	13.3	<0.08

[Guinn,1970]

TABLE 2

Tar Ball Analytical Results

ID#	ppm Dry Weight Found		
	Mn	Na	Zn
362-1	15.5 ± .32	13.9 ± .09	(80. ± 62.)
362-3	3.95 ± .30	12.7 ± .09	(94. ± 79.)
362-4	44.4 ± .39	2.67 ± .02	---
364-3	61.3 ± .62	3.83 ± .03	(65. ± 54.)
365-8	32.1 ± .37	4.82 ± .05	---
365-14	5.24 ± .25	10.4 ± .10	---
367-2	12.2 ± .76	5.94 ± .06	(166. ± 107.)
368-3	15.1 ± .77	8.64 ± .08	(176. ± 92.)

SUMMARY

Neutron activation procedures applied to a set of tar ball samples have readily demonstrated and quantitated some trace elements in tar balls. These preliminary results show that such a methodology can add to the information obtained in monitoring tar balls and their presence in various seas by further evaluating their composition. It is believed this procedure can be very useful in evaluating the ecological impact of surface films of oils and other materials present in the surface slick on marine waters (Feldman 1973a).

ACKNOWLEDGEMENTS

We are indebted to James Butler (Harvard, Department of Applied Physics) and Byron Morris (Bermuda Experimental Station) for permission to examine some of their speciments.

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DISTRIBUTION OF TAR BALLS AND NEUSTON SAMPLING IN THE GULF STREAM SYSTEM

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Significant amounts of tar balls were observed off the east coast of the United States during surveys of larvae fishes and their environment in summer 1972 and winter 1973. The principal objective of the investigation was to locate spawning areas of important recreation and commercial fishes (tunas, billfishes, bluefish, mackerels, and others) and determine the influence of the Gulf Stream system on their distribution and abundance. The area of operations extended from Cape Cod to the Caribbean.

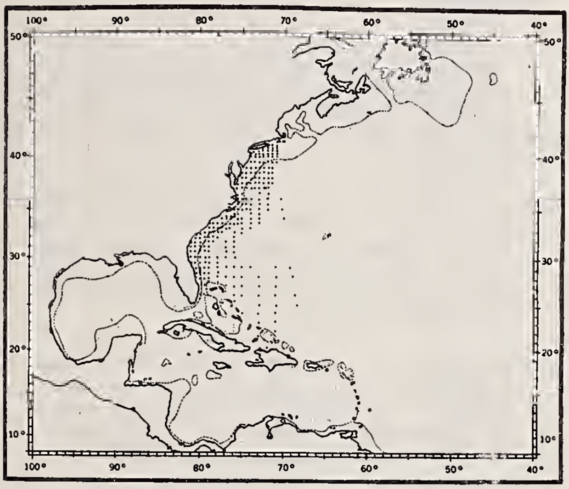

Figure 1. Location of neuston collections made during MARMAP surveys.

Vessels of the National Marine Fisheries Service (NMFS), State of South Carolina, University of Rhode Island, and the Polish Sea Fisheries Laboratory participated in the survey. Operations were conducted as part of the MARMAP program of NMFS, which is designed to systematically assess, monitor, and predict seasonal and annual changes in demersal and pelagic fish stocks.

A series of standard collections were made for fish eggs and larvae (ichthyoplankton) in the water column and at the surface. The findings described herein, are limited to the results of the surface tows for larval fish and other neuston organisms. All neuston tows were made at the air-water interface with a one by two meter neuston net at a speed of 5 knots for 10 minutes, and filtered about 3,086m^2 per tow. The net bridles were adjusted to sample in the upper half meter of water. The net used was constructed of 0.94mm mesh with a minimum ratio of mouth opening to net filtration of 1:11.

Tar balls; were observed clogging and meshes and were considered initially as a nuisance factor. However, their persistent occurrence in the samples was noted and with few exceptions they were retained for an analysis of their distribution. In the laboratory all the tar was removed and and dried weights determined in grams for each of the samples.

The amounts of tar retrieved from the samples is considered minimal. In the initial samplings some tar was discarded at sea. In heavy seas the neuston net did not effectively sample tar balls that were mixed in the upper several meters by wind-induced turbidity. And at the towing speed of 5 knots significant amounts of tar are extruded through the meshes.

TAR BALLS DISTRIBUTION

Initial results from the summer survey indicate that tar contamination of surface waters in the Northwest Atlantic is not an isolated phenomenon, but is widespread. Larval bluefish, flounder, tuna, blue marlin, and other important resource species were collected in neuston nets contaminated with tar.

Average concentration of tar balls were compared among six geographic areas; heaviest average contamination in summer, 3.9mg/m^2, was in the region north and east of the Bahamas and Antilles. Average values for the other areas did not exceed 0.8mg/m^2. Our examination of the neuston samples collected in winter (January-March 1973) from Cape Cod to the region north of the Antilles showed that tar balls were again most heavily concentrated north of the Antilles; average station value was 4.8mg/m^2. Average values for the other areas were comparatively low, 1.3mg/m^2. A summary of the weights of tar balls by station on both the summer and winter surveys is given in Table 1.

Although sampling variation has not been subjected to rigorous analyses, we noted that low tar amounts were found from offshore Virginia to Cape Cod in winter this may have been caused by a sampling bias. Unusually rough seas were encountered offshore in winter and the sampling efficiency of the neuston net is reduced when tar balls are mixed in the upper few meters in turbulent seas.

The area north and east of the Antilles sampled on both surveys represents the western boundary region of the Sargasso Sea. It is not surprising to find the heavy concentrations in this region, which is a large eddy that concentrates floating objects including Sargassum Weed. Flotsam is accumulated from the rapidly moving waters of the current about the periphery of the eddy, the Gulf Stream on the west and north, Canary Current on the east, and North Equatorial and Antilles currents to the south.

Table 1

PERCENT OCCURRENCE, AND AVERAGE CONCENTRATIONS (mg/m^2) OF TAR BY AREAS IN SUMMER 1972 (JULY-AUGUST 1972) AND WINTER 1973 (JANUARY-MARCH 1973) DURING MARMAP SURVEY OPERATIONS

SURVEY	REGION	NO. OF NEUSTON TOWS	PERCENT W/TAR	CONCENTRATION mg/m^2
S	Va-Cape Cod (coastal)	29	31	0.18
W	Va-Cape Cod (coastal)	29	38	1.04
S	Va-Cape Cod (offshore)	52	83	0.77
W	Va-Cape Cod (offshore)	51	59	0.05
S	N.C.-Florida (Gulf Stream)	32	78	0.23
W	N.C.-Florida (Gulf Stream)	48	90	1.22
S	N. Antilles & Bahamas	39	87	3.9
W	N. Antilles & Bahamas	47	96	4.8

(S-Summer & W-Winter)

COMPOSITION OF TAR BALLS

Pelagic tar from 20 samples were sent to Dr. James Butler at Harvard University, Cambridge, Massachusetts, for analysis. The samples were analyzed by low resolution gas chromatography to obtain semi-quantitative profiles of normal paraffins in the range from C12 to C35, and a quantitative indication of the relative amount of other compounds having a volatility in that same range. Two-thirds of the chromatograms showed bimodal paraffin distribution, in the C20 to C35 range characteristic of crude oil sludges. This is evidence that these tar balls come from tanker wastes dumped at sea. One sample was almost all paraffins. The samples mostly were weathered residues of waxy paraffinic crude oils, and similar with respect to the parameters measured for numerous samples collected in the Sargasso Sea near Bermuda [1].

Jeffrey et al [2], recently completed an analysis of tar balls collected with neuston nets in the Gulf of Mexico and Caribbean Sea. Extraction of pelagic tar aggregates revealed that 37 percent of tar mass was debris, including rust, wheat grains, clay, silt, and other constituents. Average concentration os debris-free tar in the Gulf and Caribbean were 0.88 and o.74 dry mg/m^2 respectively. Suspected major sources of the tars are tanker flushings on the shelf and waste dumping over the continental slope.

Petroleum residues (tar clumps) have been found throughout the Atlantic. Morris and Butler [3] estimate the standing stock at 86,000 metric tons with concentrations in the Sargasso Sea 3.6 times greater than the average wet weight of daytime zooplankton (9.4 versus $2.6 gm/m^2$). Tar clumps constituted about 20 percent of the weight of surface samples (neuston) of zooplankton collected by them in the western Atlantic on a transect taken south of the Grand Bank between 42°N and 38°N.

The effect of petroleum residues on the production cycle in the sea is not clear; laboratory investigations and in-situ investigations on phytoplankton contamination by oils are presently underway Gordon and Prouse [4]. The effects of petroleum residues on the ichthyoplankton is not understood; under laboratory conditions oil compounds extracted from oil films have been shown to be toxic to fish eggs and larvae Krunhold [5] Mironov [6].

The effects of zooplankton viability is also not clear Nelson-Smith

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ESTIMATION OF THE MODERN OIL POLLUTION OF THE NORTH ATLANTIC WATERS

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The investigations made during the 1972-73 expeditions by vessels of the USSR Hydrometeorological Service in the North Atlantic permitted estimation of the spatial and vertical distribution of oil products in waters of this, the most important region of the World ocean.

The dominant role of fluid dynamics in the distribution of these pollutants is determined. The minimum concentrations of oil products are found in midstream areas of the Gulf Stream and the North Atlantic current. The maximum concentrations are found in the peripheral regions of these circulation systems and also inside of the gyres of different types and origin. These characteristics of spatial distributions of oil pollution are presumed to be caused by processes of turbulent diffusion. The velocities of the main flows are not uniform. Observations showed that where sharp gradients are formed, intensive turbulent transfer from midstream to the periphery is caused by the cross current component. As a result, the main flow is free of oil products which are concentrated on its periphery.

The vertical distribution of oil products is characterized by greater variety, because some fractions of these pollutants have different physical characteristics, particularly, different specific gravities. The light fraction oil film probably behaves like detergents when first thrown into the sea. The vertical distribution of the heavy fractions is similar to that of mercury distribution. Finally, the emulsified and dissolved fractions are distributed regularly through the vertical water column; these distributions follow regular patterns that are dependent on specific hydrodynamic factors.

Regions adjacent to the North American and the Western European coasts are the North Atlantic areas most polluted by oil and oil products.

TOPICAL SESSION VI.
Biological Assessment

NBS Spec. Publ. 409, Marine Pollution Monitoring (Petroleum), Proceedings of a Symposium and Workshop held at NBS, Gaithersburg, Maryland, May 13-17, 1974 (Issued December 1974).

VALUE OF OIL POLLUTION MONITORING IN MARINE ORGANISMS

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The principal force motivating an international program for petroleum monitoring is undoubtedly western world opinion which recognizes the great environmental dangers of excessive voluntary or accidental discharges. The most feared environmental effects are those impairing the ocean environment, while it is understood that, in this instance, one is referring to the biological productivity of the oceans. We are therefore worried that petroleum products, or rather excessive discharges of petroleum products will impair the biological productivity of oceans, coastal areas and estuaries. To satisfy this legitimate concern, two fundamental needs must be fulfilled before monitoring can be successful. First of all, there must be monitoring of relevant or representative tainting products, which implies an identification of harmful fractions; secondly, a range of biologically or esthetically tolerable concentrations of tainting products must be established.

At present, I submit that we only have restricted knowledge of either of these conditions. In other words, we are now planning to measure hydrocarbons in water, without knowing precisely which are the most harmful and in what concentrations these products can be tolerated. We may thus be responding primarily to panic. We may also be doing something because action is better than inaction. This, in my opinion, could represent busy work which could unfortunately represent excessive expenditures once we know what to measure, how much of it can be safely tolerated by the environment. The two more positive features of monitoring can be that it will encourage the kind of international cooperation and coordination essential for the reporting system and it will keep world opinion focused on the problem as it gets more dramatic. In that same vein, there are additional dangers in setting up such a monitoring system without adequate inputs from biologists. For instance:

1- public knowledge that petroleum monitoring is underway may give a false sense of security to those who assume that, because something is being continuously measured, the danger has lessened;
2- the monitoring methods themselves may be obsolete before the tainting agents and their critical concentrations are established;
3- the deterioration of productive coastal or estuarine areas may proceed at a faster rate than the identification of harmful products are made.

At the moment, to give warning of oil slicks entering coastal waters or approaching fishing areas would be next to useless since, in all probability, the choice of contingencies could be unacceptable. For instance, the spilled oil might be: 1- dispersed, which would render it more toxic to most organisms, with the possible exception of those capable of fleeing affected areas, or, 2- attempts could be made to collect it, using current techniques; this would hardly be effective and, at best, could assist in saving some real estate or personal property values.

My proposition is that, now or in the immediate future, as the refinements of world monitoring proceed, we also must invest reasonable efforts to establish the water quality criteria for the survival of desirable ecosystems, with respect to fossil fuel hydrocarbons. In other words, what concentrations of these hydrocarbons can ecosystems safely tolerate? This still remains to be established, and will remain so until we devote enough efforts in this direction. At present, Annexe V and its appendices represent logical structures for reporting, but again, these structures are resting on shifting sand, if I may use the metaphor. It is not until we know the quality and quantity of material to be detected that we can realistically report dangers to the environment.

Presently, one of the favored demonstrations of toxicity to various marine species is a test, referred to as the TL50 or LD50, whereby animals are submitted to products for a period of 96 hrs. under artificial conditions. On one hand, it should be stressed that the 96-hr. LD50 is not a legitimate evaluation of product toxicity since it deals primarily on a scale of life or death over an arbitrary period of 96 hours of exposure. On the other hand, the test can be useful in establishing concentrations of test products to be used in long-term experimental exposures aimed at identifying subtle but significant biological impairments. This latter type of experimental work would mean that concerted interdisciplinary work would evaluate the chronic impact of oils on key species. In these studies, continual monitoring of pollutants, with time, is important. Chronic exposures would thus be coupled to systematic detection schemes for the evaluation of anomalous developments in larval, intermediary or adult forms. The approach would, of course, represent sizeable expenditures. However, it is doubtful that any real progress will be made unless significant biological anomalies can be related to pollutants in realistic concentrations, over realistic periods of time and under realistic conditions.

Recently, the Marine Technology Society has sponsored a workshop of scientists from several disciplines and belonging to three important sectors of society: the university community, the government and industry. This interdisciplinary group, including behaviorists, engineers, chemists, biochemists, pathologists, biologists, etc., will develop experimental approaches whereby various coastal ecosystems will be studied to evaluate the extent and significance of biological damage caused by pollutants, alone or in realistic combinations. The evaluation studies would be made in the classical manner, that is, in all instances, controls would be examined at regular intervals and compared to exposed organisms.

Various aspects of probable changes would then be made. In a first tense, gross evaluations would be made on pigmentary responses, ectoparasite distributions and diversities, oxygen consumption, swimming performances, gross behavioral anomalies, etc. In a second step, early or obvious changes would be pursued by more probing tests which would include blood counts, biophysical properties and enzymology, followed by histopathology, histochemistry and cytopathology. Studies would attempt to identify morphological, functional or developmental anomalies directly related to specific pollutant exposures, under realistic and adequately monitored conditions. Probable synergistic and antagonistic effects of pollutants would receive attention in experimental programs as similar to normal environmental conditions as can be effectively attained. In associated studies, evaluation of contamination and decontamination rates of various tissues would be made. Estimates of metabolic transformations and increased contamination of predators would receive attention. This would, of course, provide public health impact of contaminated organisms.

In the development of experimental procedures, the following tasks will be assumed by the participating scientists. First, a select group of test organisms will be developed; in general, the species chosen will have been extensively studied by scientists in the past. Secondly, there will be a need to establish the environmental parameter ranges these species can be expected to normally withstand; thirdly, there will be a need to establish the normal range of each biological parameter of test organisms and their significance as index of well-being; fourthly, it will be necessary to establish biological parameters which provide clear indications of particular anomalies; great advantage would be derived if these indices or symptoms can be related directly to particular types of pollutants or combinations of pollutants. Finally, it will be necessary to compare the response of organisms to the environmental parameters in the presence of pollution or pathogens, or combinations of either naturally occurring diseases and abnormal concentrations of pollutants. Relationships could then be established between the biological and environmental changes of natural populations as defined experimentally. From this, it is expected that realistic tolerable levels of pollution in the environment would be identified. These levels would then be equivalent to water quality criteria to the various species studied and, as originally planned, these criteria, having been modulated by social and political requirements, would assist in the elaboration of realistic standards.

To pursue this type of experimental work, which must be verified under near-natural conditions, it is anticipated that extensive oceanographic and atmospheric information will be needed in order to simulate and understand the physical and biological interplays of various types of environmental conditions and petroleum products. Experimental work on biological systems could advantageously benefit from or serve the pilot project on marine pollution monitoring; for instance: field observations can be essential to establish realistic experimental conditions. Also, the siting or measures of definite oil concentrations resulting from spills could be related with verified experimental findings and reveal, with some accuracy, the resulting damage to particular ecosystems. The studies on pathological developments of various species would serve this same monitoring program in establishing that various concentrations of petroleum, entering certain areas, are likely to cause a specific damage, in that some or most species will be seriously impaired. Appropriate measures could be taken, such as those involving the replacement of key species after a period of time is allowed for the depuration of the affected areas. It would appear that the development of biologically compatible cleaning-up operations will have to be tested through the combined efforts of chemical-monitoring and biological testing programs. Much can be learned from spills in the environment, such as that of the Torrey Canyon and the Falmouth incidents. However, appropriate experimental work, integrated with field observations, would ensure that field measurements are relevant and that these will help in defining criteria rather than merely predict catastrophies.

For this reason, I would strongly suggest that intensive coordinated efforts be made by the world scientific community to establish the precise nature of products which are biologically damaging and how much of these can be tolerated by a viable environment. I would also recommend that Annexe V advocates close exchanges of information between monitoring and biological scientists. This could ensure that chemical monitoring will reveal the conditions necessary for the establishment and eventual enforcement of biological criteria and standards.

Key Words: marine organisms, biological productivity, water quality criteria, TL50 or LD50, long-term exposures, interdisciplinary work, test organisms.

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EFFECTS OF OILS ON BALTIC LITTORAL COMMUNITY, AS STUDIED IN AN OUTDOOR MODEL TEST SYSTEM

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Introduction

A proper evaluation of the nature and extent of biological effects caused by oil spills at sea is a necessary but difficult task. For example as pointed out by Grassle [1] there is a great uncertainty as to where in the ecosystem and by which means studies with this aim should be performed.

In the Baltic Sea ecosystem the littoral zone is of major importance. The archipelago of this inland sea comprises more than 20,000 km^2 representing about 6 % of the total area. This highly diversified zone is responsible for much of the primary production of the Baltic and constitutes food chains with endpoints in about 50 species of fish and 40 species of birds [2].

The Brown alga belt, consisting mainly of *Fucus vesiculosus* harbors about 70 % of all Baltic macrofaunal species [3,4]. Therefore it was felt pertinent to focus on the dynamics of the littoral zone when we tried to develop a test system for evaluation of effects of oil pollution in the Baltic Sea. The aim of our study was to develop a method for this type of evaluation that is convenient to use under field conditions during and after a real oil spill. The method was tested in outdoor model systems, simulating realistic littoral conditions, where the different environmental parameters could be well controlled.

Test system

Plastic swimming pools made by Cranpool were used for the model systems. The pools (water surface, 7.3 m^2, volume 4.8 m^3) were equipped with a flowthrough system providing $\sim$2.5 l/min and designed to prevent oil from leaving the system as illustrated in figure 1. The main components of the Baltic littoral ecosystem were then introduced into the pool to form a balanced model system. *Fucus vesiculosus* occupied 1/3 of the sand covered bottom. Twelve roughly equally sized plants (100-200 gr wet weight) attached to small stones were distributed amongst the rest of the *Fucus* in each basin, comprising $\sim$ 10 % of the total weight of *Fucus*. Each of these plants was placed in the middle of a folded polyethylene bag which was covered with sand. The floral and faunal elements were all collected in the neighborhood of our laboratory (90 km south of Stockholm). The systems were set up in late July and the beginning of August 1973 and allowed to stabilize prior to any experimental stress. The tests were performed during the period September, 5 - October, 26 1973. Simulation of an oil-spill was accomplished by adding a single dose, 4.8 liters (1000 ppm) of oil to the test system at zero time. This should, if evenly distributed, give an oil layer of $\sim$ 0.7 mm thickness. Three different oils were used in the test: Light fuel oil (diesel type), Medium fuel oil and Nigerian crude oil. The sampling procedure is illustrated in figure 1. At intervals two samples of *Fucus* including the faunal elements were taken from each basin. Samples were taken immediately before the addition of oil and 3, 7, 15, 33 and 54 days after zero time. In order to minimize the loss of animals during and after sampling the whole plant was immediately brought to the laboratory for examination. The wet weight of the *Fucus* was determined and only living animals were sorted and counted. The material was divided into 15 systematically defined groups.

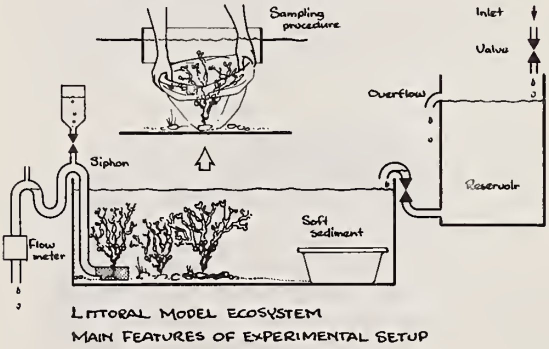


Figure 1.

Method of evaluation

As exemplified in table 1 the resulting lists of systematic groups and numbers of individuals give a somewhat confusing picture. The results from the test with light fuel oil showed more obvious effects, although much less dramatic than the visual appearance of the massive kill observed in the test. The tabulated

Table 1

	Time	Gammarus spp.	Idothea spp.	Mytilus edulis	Cardium glaucum	Theodoxus fluviatilis	Total No. of ind.	Total No. of syst. grp.	Average No. of syst. grp.
Control	A	42	15	260	444	383	1226	13	10
	B	41	31	247	242	234	871	14	12
	C	27	5	152	123	199	540	9	7
	D	38	8	124	195	175	866	11	9
	E	24	8	207	233	408	1132	13	12
	F	53	5	136	169	169	774	15	12
Medium fuel oil	A	274	133	161	306	175	1406	12	10
	B	107	63	258	687	139	2189	9	8
	C	6	9	573	265	159	1748	9	8
	D	5	55	343	382	165	2246	10	8
	E	12	30	573	184	42	961	9	7
	F	0	9	444	865	170	2068	7	6
Light fuel oil	A	56	18	152	102	213	689	11	10
	B	6	16	75	124	182	419	8	7
	C	4	21	312	216	138	752	12	9
	D	0	0	391	97	131	712	9	9
	E	0	0	67	10	95	229	6	6
	F	0	0	70	3	4	81	6	4

Average number of ind./100 g Fucus wet weight. Some of the most abundant systematic groups in samples taken during the experimental time.

results of the treatment with the less toxic medium fuel oil are much less clear. Obviously we had to find a method of evaluation giving a sufficiently detailed description of changes in community structure, e.g. by means of some biological indices. In studies on effects of water pollution, diversity indices applied on benthic faunal communities have successfully been used [5,6,7]. But this type of index requires material determined at the species level, which in this case, was considered too time consuming. For our purposes the use of affinity indices calculated from higher systematic groups was decided to be more convenient. If these selected systematic groups are defined after the actual needs it is meaningful to use such an index to assess the degree of similarity between samples. Two types of affinity indices were used, the coefficient of community and the percentage similarity of community as reviewed by Johnson and Brinkhurst [8].

The coefficient of community, CC, measures the percentage of species shared by two samples as

$$CC = \frac{c}{a + b - c} \cdot 100$$

in which a is the number of species in the first sample, b is the number of species in the second and c is the number of species occurring in both.

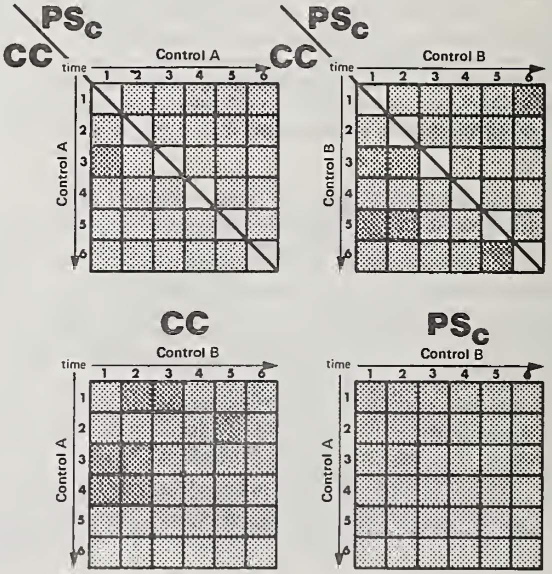
The relative abundance of species is considered in the percentage similarity of community PS_c.

$$PS_c = 100 - 0.5\Sigma(a' - b') = \Sigma \min(a', b')$$

in which a' and b' are for each species the percentages of the total number of animals in samples A and B respectively. Both indices take values between 0 and 100, which represent the lowest and highest affinity, respectively, between two samples.

Results and discussion

In figure 2 the samples from the two control basins A and B are compared in so called Trellis diagrams. The diagrams below in figure 2 show the high degree of similarity between samples taken at different times within each control basin. To check the possibility that there might be differences in community structure between basins, we compared the two replicate control systems. As illustrated below they



Stability of test system. Similarity between samples taken at six occasions from two control basins A and B (above), and between the two basins (below).

CC = COEFFICIENT OF COMMUNITY

PS_C = PERCENTAGE SIMILARITY OF COMMUNITY

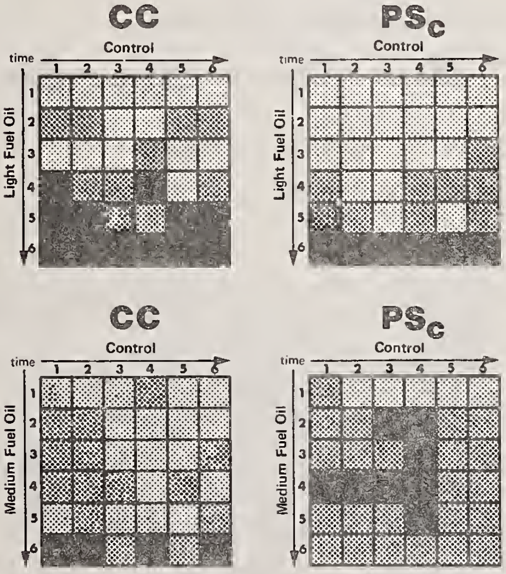
Scale ■ 0–50 % ▩ 51–65 % ▨ 66–100 %

Figure 2.

seem to be very similar. This is also the case when the first sample from the test basins is compared to the samples from the control as seen in the first row in each Trellis diagram in figure 3.

In the test with light fuel oil (fig. 3) the values of the CC index were soon strongly affected. The PS_c index, however, reacted rather slowly. The light fuel oil with its high amount of low boiling aromates and consequently high acute toxicity soon gave a complete extinction of many systematic groups of animals, and this will affect the CC index. But since the exposure to the oil reduced the number of individuals rather unspecifically and probably not caused great changes in relative composition the PS_c index is little affected during most of the test period. This unspecified affect gives in this case specific damage in the ecosystem since a lot of the less abundant groups can be completely eradicated and thus giving rise to an unbalanced ecosystem.

The Trellis diagrams from the basin with medium fuel oil (fig. 3 below) give the opposite impression. The reduction in PS_c index values is more pronounced than that of the CC index. It should be observed that this reduction is noted immediately. As the CC index seems rather unaffected we conclude that some abundant species must have been reduced but not extinguished during the test. This could be explained if we assume that some chemical or physical property of the oil changes during the test period. For example a reduced stickiness of the oil surface or lower dissolution due to the formation of a water in oil emulsion. Since the Nigerian crude oil gave an intermediary picture compared to the tests on light fuel and medium fuel oil it has been excluded in this presentation.



Effects of oils on the littoral community in the model test system
Changes in faunal affinity as comapred to the control basin

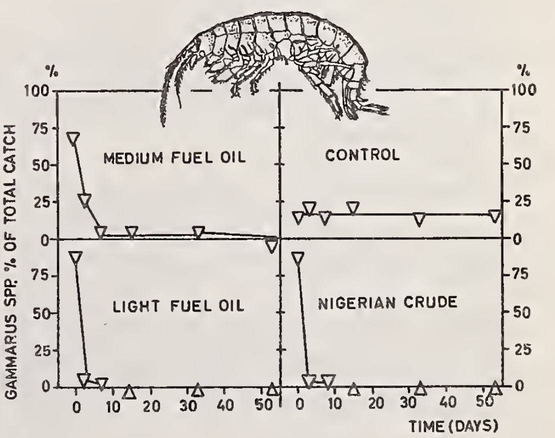
CC = COEFFICIENT OF COMMUNITY
PS_C = PERCENTAGE SIMILARITY OF COMMUNITY

Scale ▓ 0–50 % ▒ 51–65 % ░ 66–100 %

Figure 3.

The crustacean group Gammarus spp can be used to illustrate the different effects of the tested oils. Most crustaceans have a body surface with a cuticle which is covered with a hydrophobic wax layer [9]. In Gammarids this is very pronounced and these animals are therefore very sensitive to lipophilic substances. As seen in figure 4 all three oils cause a rapid reduction in numbers of individuals in the samples. But while in the light fuel and Nigerian crude oil the Gammarids are completely extinguished after one week they are present in the medium fuel oil throughout the test period. In the control the abundance of Gammarus spp is relativele constant with time.

In the experiments the animals were prevented from leaving the basins and thus the results obtained could be far too drastic compared to those obtainable under field conditions. We therefore checked this on a number of samples of the Fucus attached fauna gathered in the field. In October 1970 the small bay of Gästviken in the Stockholm archipelago was



REDUCTION OF GAMMARUS SPP. IN FUCUS SAMPLES FOLLOWING OIL SPILLS.

Figure 4.

polluted by a massive oil spill. Approximately 400 tons of medium and heavy fuel oil drifted into the bay under a strong wind. The Swedish coastguard managed to enclose the oilslick with bars across the Bay. Most of the oil was then collected mechanically during the winter, and in the middle of May 1971 the operations were finished. During this year Fucus samples were taken on four occasions and on one occasion the following year as part of a recovery study in the area. In 1971 single samples were taken in June, July and November at two stations in the bay (A and B). In a nearby unpolluted bay (R) one sample was taken in July 1971, and was used as a reference point (fig. 5). In July 1972 three samples were taken at both station A and B. The method used was similar to the one described for the test system. In this case the algae were enclosed in the plastic bag from above before the plant was cut off the rock at the ritsom region.

The samples taken gave us the opportunity to compare the samples from the polluted bay in the first year (1971) to references in time and space, namely the 1972 samples from the stations in the bay and the 1971 R sample. As seen in figure 5 the two stations A and B react in a similar way. When comparing the June 1972 samples to the samples taken in June, July, August and November 1971 a very low similarity to the first months can be observed. In August, however, the higher affinity seen especially in the PS_c index must be attributed to a recovery by migration of dominant species into the bay.

If the 1971 samples from station A and B in Gästviken are compared to a sample from the reference station R in July the same year, the pattern is identical. Note that in both these comparisons the PS_c indices are the most affected which might have been expected since this also was the case in the test system with medium fuel oil.

As seen in figure 5 above it seems that the sampling method is rather accurate since the affinity between the three subsamples in June 1972 is high.

In conclusion we have found the above described method of using changes in the structure of Fucus communities both rapid and sensitive in measuring effects due to oil pollution in the Baltic littoral fauna.

Acknowledgement:

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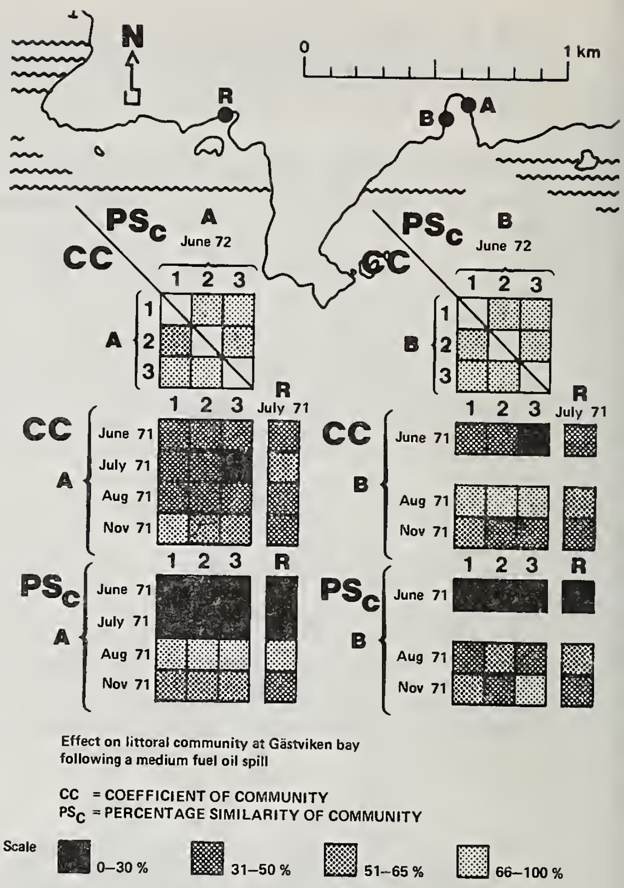

Effect on littoral community at Gästviken bay following a medium fuel oil spill

CC = COEFFICIENT OF COMMUNITY
PS_C = PERCENTAGE SIMILARITY OF COMMUNITY

Figure 5.

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Key words: Affinity indices; Baltic littoral community; field study; model test system; oil spill; toxicity.

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HYDROCARBON CONTENT AND CHLOROPHYLL CORRELATION IN THE WATERS BETWEEN NOVA SCOTIA AND THE GULF STREAM

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Several laboratory experiments have shown that phytoplankton produce hydrocarbon material [1, 2, 3, 4]. Therefore one would expect that a certain amount of the hydrocarbon material found in the marine environment is from this source and that a correlation between hydrocarbon content and chlorophyll should be present. The author has found this to be true in the euphotic zone of the upwelling waters off Northwest Africa [5]. One drawback to the data that was accumulated there was the fact that the method used was not capable of providing the absolute values for the hydrocarbon concentrations and the values given were purely relative ones. This is unimportant in a correlation study dealing with one particular region but can be a serious handicap in comparing one region to another. In this study it was possible to use an improved method, which enabled the absolute concentrations to be determined in a body of water with considerably different hydrographic properties from the upwelling water.

The samples were taken on the CSS DAWSON in the euphotic zone at 1, 10, and 25 m at 8 stations during a cruise toward the end of July 1973. The stations were on a line that went almost due south from Nova Scotia to the Gulf Stream. The method used is described in greater detail in another part of this volume and in the literature[6]. It consisted of extracting 1 liter of the sea water sample with a non-polar solvent at sea and then concentrating the extract in the laboratory. The hydrocarbons were separated from non-hydrocarbon material by means of high performance liquid chromatography and were then detected by a flow calorimeter. Duplicate samples were run whenever possible and blank values subtracted. Each value had a standard deviation of ± 3.1 µg/l.

The chlorophyll content was determined at the AOL laboratories of the Bedford Institute by the fluoremetric method.

The average value for the hydrocarbons that was found was: 4.9 ± 0.92 µg/l with a range of -3.7 to 13.6. For chlorophyll a, it was 0.19 ± 0.036 µg/l with a range of 0.02 to 0.813. The average hydrocarbon content was considerably lower than that found by the author in the Baltic [7], where the saturated hydrocarbons alone had an average concentration of 8.9 ± 2.0µg/l.

Curves of estimation with significant correlation (P under 0.05) were found between hydrocarbon and chlorophyll content with, linear, logarithmic, quadratic, and hyperbolic equations. The estimating equation that was decided on was in the form: $Y = a + b \log (1 + C)$. This equation was felt to be the most suitable for two reasons. It intersects the Y-axis when $C = 0$, thus enabling an estimate to be made of the amount of anthropogenic hydrocarbon material present, and, secondly, in it the rate of change in the hydrocarbon concentration decreases greatly as the chlorophyll concentrations become high. This is to be expected, since a feedback condition almost certainly exists between the amount of phytoplankton and the concentration of hydrocarbon material. Although a larger phytoplankton population would result in a greater production of hydrocarbon material, it should also result in a larger amount of particulate material upon which the hydrocarbons can adsorb [8] and then be removed from the system by either sinking or grazing. The estimating equation found was:

$$\text{Hydrocarbons } (\mu g/l) = 1.7 + 41.45 \log (1 + \text{Chlorophyll } (\mu g/l))$$

$$r = 0.54$$

$$t = 3.0 \qquad 0.005 < P < 0.01$$

$$s_{Y.X} = \pm 3.6$$

$$N = 23$$

Where r is the correlation coefficient, t is the result of a "t" test made on it, $s_{Y.X}$ is the standard error of estimate, and N is the number of samples. The correlation coefficient is not very high, but the "t" test shows that the probability of obtaining a correlation coefficient of that magnitude due to chance is only possible in less than 1 case out of 100. In a process as complicated as the one being considered here, this is quite significant. The amount of material that is presumably anthropogenic is 1.7 ± 3.6 µg/l. This is of course only a rough estimate due to the high standard of error, but it does suggest that anthropogenic material was present in the waters tested. In the future more data should be accumulated to make this estimate more precise. A similar analysis of the data from Northwest Africa results in:

Hydrocarbons (relative units) $= -0.1 + 8.41 \log (1+C)$

$r = 0.67$

$t = 6.8 \qquad P \ll 0.001$

$s_{Y.X} = \pm 1.5$

$N = 58$

The slopes in the two equations cannot be compared due to different units used. The two correlation coefficients do not differ significantly [9] , but due to the greater sample size, the value off Africa is far more significant. The amount of anthropogenic material would be -0.1 ± 1.5 μg/l, suggesting that the waters there were free from pollution. This is reasonable, since upwelled water has been on the surface for only a short period of time and is unlikely to have been contaminated. In addition, sampling was done close inshore away from any tanker routes.

The average value for chlorophyll that was found in the euphotic zone off Northwest Africa was 3.5 μg/l. If one assumes no pollution and applies the estimating equation found for the ocean south of Canada, one would expect to find on an average about 27 μg/l of hydrocarbon material off Northwest Africa in the euphotic zone.

Both these studies have indicated that a casual relationship exists between the hydrocarbon and chlorophyll concentrations in the euphotic zones. Naturally one cannot assume that phytoplankton is the sole source of this material. An increase in the phytoplankton population will also result in an increase in other members of the ecosystem such as the zooplankton, and these too might be introducing hydrocarbon material. Independent of this, there also appears to be hydrocarbon material in the ocean to the south of Canada, which presumably is anthropogenic and is absent in the upwelled water off Northwest Africa.

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EFFECT OF AN OIL SPILL ON BENTHIC ANIMALS IN THE LOWER YORK RIVER, VIRGINIA[1]

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Introduction

Although considerable study has been centered upon intertidal organisms with respect to their response to oil spills, most investigations have been conducted on exposed rocky intertidal habitats (1). Few studies are available which describe the response of benthic animal communities in mid-Atlantic estuaries and particularly in its largest estuary, Chesapeake Bay. This study documents both from field survey data and laboratory bioassay studies the effects of an accidental oil spill on the intertidal benthic communities of the Lower York River, Virginia.

Field Study

On 5 May 1971, a number of slicks of oil (cracking residue thinned with No. 2 fuel oil to the consistency of No. 6 fuel oil) washed onto the sand beaches and Spartina marshes near the mouth of the York River. To assess the effect that this event had on the intertidal organisms of these beaches, a series of transects was established at three locations in this area and sampled during July and December of 1971, March of 1972 and April of 1973. One transect of samples (station no. 2) was collected where a slick came ashore, while two transects of samples were taken in unaffected areas (stations no. 1 and no. 3). Station no. 1 is approximately 1.14 nautical miles upriver from no. 2 and no. 3 is approximately 0.79 nautical miles downriver from no. 2 (fig. 1).

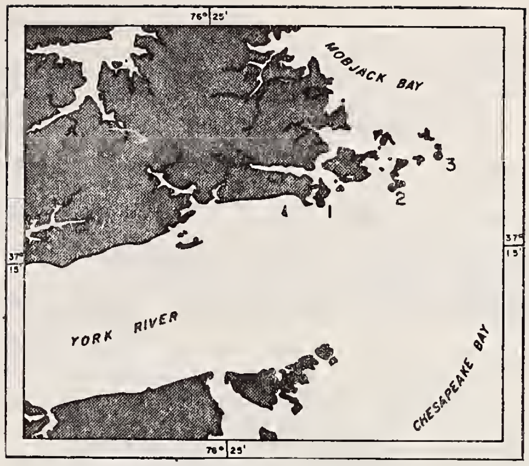

Figure 1. Location of Sampling Stations

The procedure on each transect involved making a subjective determination of the width of the intertidal zone and then setting up five equally spaced substations within this zone. A series of ten samples was then taken to a depth of 15 cm with a plexiglass corer (0.0069 m^2) at each substation. The cores were sieved through a 1.0 mm screen and the material remaining on the screen was preserved in formalin that had been diluted with seawater and returned to the laboratory for identification and enumeration.

During the study period, 94 species of benthic organisms were collected. The major fauna were distributed as follows: 29 species of polychaetes; 28 of crustaceans and 23 of molluscs.

To numerically describe the faunal assemblages, several techniques of community structure analysis were employed. These included species richness, evenness, information theory diversity, and the use of Sorenson's quotient of similarity (2).

The number of species, individuals, and values for richness, evenness and diversity calculated on the samples during the study are tabulated in table I. Figures 2 and 3 show the change in richness and diversity as a function of time. Figure 4 graphically depicts the change in Sorenson's similarity quotient as a function of station comparisons and time.

The effect of the spill is most evident when comparing numbers of species or species richness. The control stations averaged 33 species in July after the spill while the spill station had only 14. The effects of the spill were prolonged through the next two sampling periods, in December 1971 and March 1972. Recovery in terms of both species richness and faunal similarity was shown in the April 1973 study period. However, the number of individuals remained lower at the spill station than at the control stations, suggesting that complete recovery had not yet occurred. The groups

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[1] This study was supported in part by a grant from the Environmental Protection Agency (150-80-EJO).

[2] VIMS Contribution No. 623.

Table I. Community Composition Parameters

	Station 1				Station 2				Station 3			
	7-71	12-71	3-72	4-73	7-71	12-71	3-72	4-73	7-71	12-71	3-72	4-73
No. Indi.	482	536	300	231	88	107	144	153	611	2481	1757	3753
No. Sp.	32	34	35	21	14	19	13	22	34	60	46	37
Richness	5.02	5.25	5.96	3.67	2.90	3.85	2.41	4.17	5.14	7.55	6.02	4.39
Diversity	3.02	3.21	3.63	3.00	3.28	3.21	1.85	3.25	3.02	4.04	3.29	2.67
Evenness	0.60	0.63	0.71	0.68	0.86	0.76	0.50	0.73	0.59	0.68	0.60	0.51

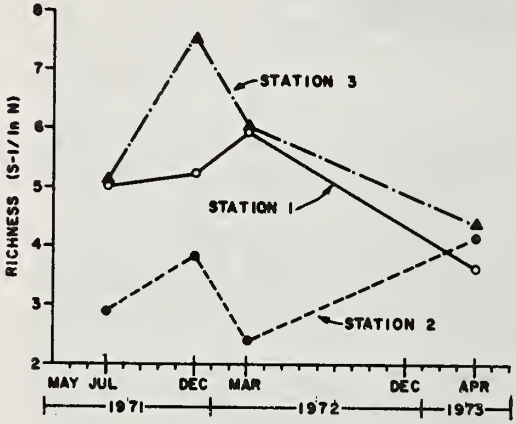

Figure 2. Species Richness

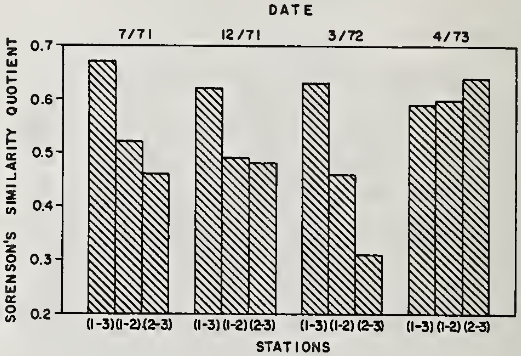

Figure 4. Sorenson's Similarity Quotient

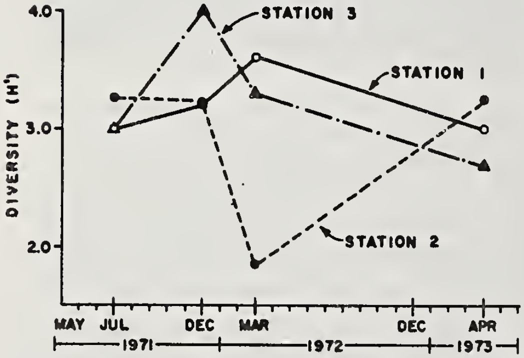

Figure 3. Species Diversity

most seriously affected by the spill were the crustaceans and polychaetes.

Laboratory Studies

After preliminary analysis of the field data showed a significant effect of the oil on intertidal organisms in the Lower York River, it was decided to conduct acute bioassays with the oil and attempt to relate the toxicities to the effects observed in the field. Unfortunately, no samples of the oil spilled had been taken; therefore, it was decided to assay Bunker C because of its close resemblance to the oil spilled and because of its extensive use as vessel, industrial and utility fuels.

The test organisms included Spiochaetopterus costarum oculatus (Polychaeta), Nereis succinea (Polychaeta), Nassarius obsoletus (Gastropoda), Modiolus demissus (Bivalvia), Edotea triloba (Isopoda), Gammarus mucronatus (Amphipoda) and Pagurus longicarpus (Decapoda). The organisms were chosen because they appeared as York River dominants (3), (4) and because they represented major taxonomic divisions of York River intertidal macrofauna.

Only the toxicity of the water-accommodated components of Bunker C rather than the residue, was assessed in the study. The dosing apparatus used was a closed continuous flow system, where pumps delivered various dilutions of an equilibrated oil in water solution to flasks in which the test animals were placed. Quantitative estimates of the oil were made using infrared spectroscopy (5).

The test organisms were subjected to five concentrations of oil with a control. The tests were conducted for 48 hours at salinities ranging from 12 to 18‰. Duplicate tests were conducted with each organism. The total dissolved organic content of the equilibrated oil and water solution was 5.53 ppm. Frankenfeld (5) previously reported only 1.9 ppm water extractable organic compounds from a No. 6 fuel oil. The difference between the two results may be that during his study, solutions of oil and water were not agitated. In this study mechanical agitation was used. However, no "solutions" were tested before all visible oil had appeared to float to the surface.

In the replicated experiments neither *N. obsoletus*, *E. triloba*, *N. succinea*, nor *M. denissus* showed mortality which could be attributed to the presence of oil, while in all assays *G. mucronatus*, *P. longicarpus* and *S. costarum oculatus* displayed patterns of mortality from which TL$_{50}$ values could be determined. The 48 hour TL$_{50}$ values were 0.42 ppm for *G. mucronatus*, 0.62 ppm for *P. longicarpus* and 4.92 for *S. costarum oculatus*.

Further details concerning the bioassay tests can be found in Hyland (6).

Discussion

The four species which were not affected by accommodated oil in the laboratory also did not reveal population depressions following the oil spill in the river. The tolerance displayed by *N. obsoletus* and *M. demissus* may reflect a general resistance of molluscs to acute oil toxicity as suggested by Mironov (7) and Moore, Dwyer and Katz (8). It should be mentioned, however, that molluscs may be susceptible to other adverse effects, e.g. as Scarrat, Sprague, Wilder and Zitko (9) have demonstrated the ability of *M. modiolus* to concentrate various fractions of Bunker C. In addition the toxicity of dissolved oils should be tested for larval molluscs before such a generalization should be made.

It is not understood why *Edotea* was tolerant to the oil, since the two other crustaceans tested were quite sensitive, both having TL$_{50}$'s under 1 ppm. Unfortunately, our field sampling techniques did not allow for the capture of the hermit crab (*P. longicarpus*) which was shown to be the most sensitive species. *Spiochaetopterus* for which acute toxicity was shown exhibited the most drastic population reduction in the field study.

Species richness and faunal similarity appeared to give a better indication of the effects of the oil than did the informational diversity calculations.

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Key Words: Acute toxicity; Benthic animals; Oil; Response

NBS Spec. Publ. 409, Marine Pollution Monitoring (Petroleum), Proceedings of a Symposium and Workshop held at NBS, Gaithersburg, Maryland, May 13-17, 1974 (Issued December 1974).

MARINE POLLUTION BY CARCINOGENIC HYDROCARBONS

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Polycyclic aromatic hydrocarbons (PAH) associated with the use of petroleum and coal, the burning of refuse, and the production of coke have caused great concern as an atmospheric pollutant related to increased incidence of lung cancer. PAH's are also being studied in cigarette smoke, some foods, soil, and water. PAH contamination of seafood due to ocean oil pollution, however, has received very little attention.

PAH Content of Petroleum

The literature contains only the beginningsof an adequate study of the carcinogenic content of petroleum crudes and products. Partly because of inadequate analytical techniques, components boiling over 325°C have not been as thoroughly studied as the lower boiling fractions. According to Horton *et al.*, PAH are appreciably higher in fractions boiling above 354°C than in crude stocks (1).

Carruthers and Douglas in 1961 isolated 1,2-benzanthracene from uncracked fractions of Kuwait petroleum. Also isolated in Kuwait crude were chrysene, fluorene, phenanthrene, and dibenzthiophene (2). Graf and Winter made quantitative measures of benz(a)pyrene (BP) in crude oils from the Persian Gulf, Libya, and Venezuela. Levels were 400, 1320, and 1,600 μg/kg respectively (3).

Crude oil PAH are estimated to be on the order of 1 percent of total crude. A Bureau of Mines analysis of a Gach Saran crude found PAH in the 370-535 °C range to be 3.54 percent of the total crude (4).

The amount of carcinogenic hydrocarbons is increased by refining processes that involve catalytic cracking and reforming. The following table shows the aromatic increases from representative operations (5):

Process	Charge	% before	%after
Cat. cracking Gulf Res. Co.	Kuwait Gas Oil	22.3	40.0
Cat. reform. Houdry Air Pr.	Naptha	18.8	56.4
Cat. reform.	Arabian	10.5	66.2

Esso Research and Engineering Co. analyzed commercial grades of gasoline and found BP content ranging up to 3,120 μg/kg. Nationwide composite premium contained 480 μg/kg while regular contained 212 μg/kg (6).

Another source of high PAH is spent petroleum products. The BP content of unused motor oil was 26 μg/kg as compared with 5,800 μg/kg BP in the oil after being used in an engine for about 1,400 miles(7).

Estimate of PAH Discharged into the Ocean

The best estimates indicate that over half of total petroleum discharge into the ocean is petroleum product, not crude oil. According to Porricelli (8), marine operations (excluding offshore operations) account for 47.1 percent of total petroleum discharged. The American Institute of Merchant Shipping estimates that ten percent of world tanker trade is light product (9). Thus, marine operations with light product probably account for 4.7 percent of total marine pollution.

(This estimate is conservative. Most transport estimates consider international trade only and neglect intracoastal trade. For U.S. petroleum shipping, for example, intracoastal trade amounts to approximately 43 percent of all shipments (10). A good deal of this intracoastal trade is product. Excluding intracoastal trade from total petroleum shipping calculations gives the result that product accounts for only 46 percent of total transport; including intracoastal trade causes that figure to jump to 55 percent. This would raise the percentage of marine pollution caused by product.)

According to Porricelli, refineries, petrochemical plants, and industrial machinery, if we assume they discharge only product, add 21.4 percent of product to the 4.7 percent by marine operations. Motor vehicle pollution, all product, adds another 29.4 percent making 55.5 percent of all petroleum discharge into the ocean that is product.

If we use Porricelli's estimate of 5 million tons as total petroleum input and if we assume that all crude has a BP content of 400 to 1600 μg/kg, that non-automotive product is 1600-6400 μg/kg, and that motor vehicle discharge is 5800 μg/kg, we get annual BP input of 10 to 20 metric tons.

Comparison of BP in Seafood and in Other Foods

Numerous reports have been published on the presence of carcinogenic PAH in marine and fresh waters as well as in a variety of natural and processed food products. The following estimates that are unfootnoted come from reviews by

Andelman and Suess (11), and ZoBell (12).

The general range of carcinogenic PAH in ground water and treated surface water is between 0.001 and 0.025 μg/l. BP was found in lettuce at a maximum concentration of 12.8 μg/kg. FDA surveys of vegetable oils have found BP levels from 0.4 to 1.5 μg/kg (13). Another study found BP content as high as 48.4 μg/kg in cocoanut oil.

Grimmer found that BP in 23 samples of cereal grain varied from 0.2 to 0.4 μg/kg. Water extracted from 1 kilogram of tea contained about 4 μg of BP; 11 samples of coffee contained hardly any hydrocarbons at all (although BP has been found in roasted coffee beans).

Lijinsky and Shubik report 8 μg/kg of BP in smoked salmon, 6 to 10 μg/kg in barbecued ribs and charcoal broiled steaks, and Gorelova and Dikun found up to 10.5 μg/kg in home-smoked sausages.

Concentrations of BP in marine animals vary quite widely from nil to over 2000 μg/kg:

Sample	Location	BP content
Cod fish	Greenland	15
molluscs	"	60
holothurians	"	nil
mussels	"	18-55
crustaceans	Arctic Ocean	nil to 230
mussels	Bay of Naples	11-540
molluscs	"	2.4
sardines	"	65
various fish	Italy, Adriatic Coast	nil-900
invertebrates	"	nil-2200
shrimp mussels oysters, etc.	France	nil-90
oysters	France, Atlantic Coast	0.4-3.5 μg/doz.
oysters	France, Channel Coast	70-112
mussels	France, Toulon	16-22
oysters	French Coast	1-70
holothurians	"	up to 2000
fish & crus.	"	nil-400
fish & shell fish	"	3-155
oysters	Alabama	24
oysters	Virginia	2-6

Thus, the amount of BP in seafood is appreciably higher than amounts in non-marine food. The higher values found in marine foods are undoubtedly due to petroleum contamination from neighboring sources. The presence of relatively high levels in the Arctic Ocean and off Greenland indicate possibly high levels of BP in the entire world ocean. This indicates a strong need to monitor PAH levels, especially near major sources of pollution and near fishing grounds.

Is Oily Taste Any Protection?

The question arises as to whether petroleum contamination of seafood produces an oily taste that would prevent anyone from eating that seafood. Only a relatively small fraction of petroleum has a pronounced odor or taste. Moreover, marine animals removed from contaminated areas may not purge themselves of PAH. Blumer and his co-workers at Woods Hole suggested that petroleum hydrocarbons may persist for long periods after contamination, perhaps for the lifetime of the animal (14).

Two studies sponsored by the American Petroleum Institute are somewhat inconsistent with Blumer's results. The first, by J.W. Anderson found that maintenance in clean water for periods of from 24 to 52 days is sufficient to cleanse the tissues of detectable levels of hydrocarbons (15). The second, by Battelle Labs also found rapid (within two weeks) purging by oysters of Kuwait Crude oil (16).

Lee *et al*. studied the uptake and discharge of four toxic or carcinogenic hydrocarbons by the marine mussel *Mytilus edulis*. The mussle did not metabolize any of the compounds and, while transfer of the mussel from contaminated to fresh water did cause discharge of most of the hydrocarbons, significant amounts (1 to 400 μg/mussel) remained two weeks after the transfer (17).

Teal and Stegeman at Woods Hole found similar hydrocarbon discharge behavior in oysters (18). No. 2 fuel oil was accumulated by oysters after a 49 day exposure at a rate dependent on their lipid weight and was then partly discharged upon transfer of the animals to fresh sea water. The residue of accumulated hydrocarbons amounted to over thirty times that found in the oysters prior to exposure; the authors suggest the stored hydrocarbons represent a new equilibrium concentration of hydrocarbons in the organism or may be retained in a stable compartment.

Thus, while knowledge about the persistence of PAH in contaminated seafood is far from complete, it is clear that relying on oily taste in seafood as a danger warning is not warranted by the studies conducted on this issue. Only objective chemical analysis and not subjective taste can reveal the presence of some carcinogenic hydrocarbons. Again, this stresses the need for monitoring of PAH levels in fishing areas and in contaminated offshore areas.

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AUTHOR INDEX (Contributed Papers)

KEY WORD INDEX

Entries were taken from the key words given by authors of the contributed papers printed herein. Reference is only to first author of each paper. This index is not exhaustive; however, it should serve as a subject guide.

REPORT

of the

WORKSHOP ON MARINE POLLUTION MONITORING

held at

Gaithersburg, Maryland, USA

(16-17 May 1974)

These areas are chosen to be suitable for initiation of the Pilot Project, Integrated Global Oceanic Station System (IGOSS).

INTRODUCTION

The International Symposium and Workshop was prompted by the recognized need to communicate and exchange ideas and results, on an international basis, which reflect the status of current methodology for making measurements of petroleum and petroleum products in the marine environment. Such needs arose as the Intergovernmental Oceanographic Commission and the World Meteorological Organization decided to establish an operational Pilot Project for Marine Pollution Monitoring which was initially to focus on petroleum hydrocarbons within the framework of the Integrated Global Ocean Station System (IGOSS) programme. The outline of the Operational Plan on the above Pilot Project on Marine Pollution Monitoring and implementation programme were prepared by the Joint IOC/WMO Planning Group for IGOSS at its second session (13-17 August 1973) and subsequently endorsed by the Eighth Session of the IOC Assembly (Res. VIII-20), and the 25th session of the WMO Executive Committee (Res. 14).

The objectives of the Workshop were: (a) to provide scientific and technical advice, based mainly on information supplied by the Symposium, as to methodology (observation and reporting, sampling, sample preservation, analysis, standards criteria, data handling) to be used or initiated during the Pilot Project, and also to identify future studies needed to expand the Pilot Project; (b) to recommend technical assistance programs and training and education projects that would provide pertinent support to developing countries to enable them to establish marine pollution monitoring activities.

Results of the discussion on the above matter as well as conclusions and recommendations on the Operational Plan for the Pilot Project and further studies and actions required for its development are contained in this report.

GENERAL CONCLUSIONS ON THE PILOT PROJECT ON MARINE POLLUTION MONITORING

When reviewing the Operational Plan on the Pilot Project on Marine Pollution Monitoring and results of the discussion at the Symposium on marine pollution (petroleum) monitoring, the Workshop agreed that the basic objectives for the Pilot Project were the following:

- To initiate and expand an internationally coordinated programme for marine pollution monitoring, initially in selected areas, in order to acquire and exchange among nations intercomparable data for making periodic assessments of the state and degrees of contamination of the marine environment by oil and petroleum constituents;

- to establish the necessary organizational machinery required for further development and expansion of marine pollution monitoring.

Taking into account the fact that a significant period of time will be required for nations to prepare themselves for appropriate use of the recommended procedures and methods within the Pilot Project, as well as to train personnel on procedures for sampling, preservation and analysis, to prepare national guides and instructions, the Workshop proposed to start implementation of the operational phase of the Pilot Project in accordance with the recommended procedures on January 1, 1975. Therefore the Preparatory Implementation Phase to complete the required preparatory work should be conducted within the period of time June 1974 to January 1975.

The Workshop also proposed that one year after the initiation of the work, namely January 1976, an evaluation of progress of the Pilot Project should be conducted with the view to its further development. To this purpose, the second Workshop of national coordinators and laboratory directors as well as data managers should be convened in January 1976.

The Workshop considered existing and planned national regional marine pollution monitoring programmes and took into account recommendations of the 4th Session of the IOC Group of Experts on Oceanographic Research as it relates to IGOSS (April 1974), on the expansion of the area for the Pilot Project. The Workshop recommended inclusion, in addition to the areas recommended by the IPLAN-II for the Pilot Project, the Norwegian Sea, the ocean areas around Japan, and the northern part of the Indian Ocean.

Other conclusions and recommendations supplied by the Workshop are given in the following:

OIL SLICKS, TAR BALLS AND PARTICULATES
SAMPLING METHODS AND TECHNIQUES: ANALYTICAL METHODS

Chairmen: Mr. T. Thompson
Mr. M. Gruenfeld
Rapporteur: Mr. B. Thompson

General Comments on the Operational Plan of the Pilot Project

The sessions, in light of present technological capabilities, were in general agreement with the Operational Plan. Some changes in the sampling, analysis and reporting procedures were recommended and it was strongly urged that the projected analysis scheme be simplified and that a beach monitoring program be considered in addition to the visual and Neuston net means of acquiring data.

Methodology

(1) Visual - The sessions considered that the use of Polarizers in detecting oil slick was very effective, both from ships and aircraft.

(2) Neuston nets (Tar Balls) - The sessions supported the collection of information on Tar Balls through the use of Neuston nets and suggested several sampling procedure changes that should improve the data collection. The recommended changes are:

(a) Tow at speeds that permit the sampler to ride smoothly on the ocean surface (3-8 kts).

(b) Where suitable equipment is available, a flow meter should be employed to estimate the water scavenged.

(c) Sample during day or night, recognizing that daytime sampling will reduce the amount of zooplankton collected.

(d) Where possible, tow the net on the lee side of the vessel, and avoid heading into the wind (to minimize towing along or between windrows).

(3) Tar ball sampling on beaches - It was agreed that this method would prove useful as a complement to Neuston nets tows, in particular in areas where few research vessels are available. It was suggested that locations along the African coast would be appropriate for beach monitoring of oil spills along the tanker routes. Such sampling would have to be carried out over an extended period (at least a year) to cover seasonal variability (upwelling, monsoon, etc.). The Pilot Project should include a beach monitoring program at the earliest practicable date. It is recommended that the draft programme specifications given in Annex I should be reviewed by appropriate experts prior to issuance as program guidelines.

(4) Sample preservation - The session felt that the addition of sodium azide (NaN_3) to tar ball samples is not desirable. Refrigeration, as well as freezing, should be suggested in the operational plan. The sentence, "Screw caps should be lined with tin foil when teflon liners are not available" should be added to paragraph 3, Appendix II of the Operational Plan.

Data Handling

Forms for reporting

The Workshop suggested some modifications to the format(s) as given in the Operational Plan for the Pilot Project and recommended that the Joint Task Team refine the reporting forms and include these incorporations in the final version of the Operational Plan for the Pilot Project.

Complementary environmental data should be reported in the adopted IGOSS code forms, e.g., BATHY and TESAC code. This would ensure that all parameters would be compatible and the observation techniques fully explained.

The log form for sampling and reporting of particulate petroleum residues (tar balls) should be revised to include all the information contained in the recommended bottle label. As a minimum, an identification number, identifying the sample on the log, should be clearly marked on the bottle and the bottle top as well. Ideally, a label and log form should be used.

Data Collection

The sessions recommended that the National Coordinators arrange that all forms be forwarded to the IGOSS Responsible National Oceanographic Data Center (RNODC) for generation of statistical summaries and archival purposes. The IODE *ad hoc* Group on IGOSS Data Archiving and Exchange should be instructed to prepare a supplement for the Manual on IGOSS Data Archiving and Exchange, outline Marine Pollution Monitoring Pilot Project archival arrangements.

Supporting Studies for Expansion and Further Development

Guides and Manuals

It was further recommended that the Operational Plan be used by participating nations as instructions, or guides, for use during the first stage of the Pilot Project. International guides and instructions will be considered after the first stage. Such guides and manuals should be simple and, as far as possible, in conformity with the existing WMO and IOC guides and manuals.

New Techniques - Various new techniques and developments were presented at the session. It is proposed that they be kept under review by the Joint IOC/WMO IGOSS Group of Experts and further considered when they become operational. These include:

(a) Remote sensing techniques

Multispectral Scanners (MSS)
Infrared and Ultraviolet Oil Monitors
Airborne Laser Systems
Microwave Instruments

(b) Improved simplified surface collection and observation techniques

Platforms

Fishing vessels were judged as useful platforms for, in particular, visual observations. It was proposed that National Coordinators encourage the participation of an increasing number of ocean going fishing vessels in the Pilot Project.

Tar Sampling on Beaches

Selection of Area

(1) Minimum of human activity;
(2) No local sources of petroleum pollution;
(3) Uniformity of shoreline (no breakwaters or cuts);
(4) Sandy beach;
(5) Gentle slope should be present but not so as to make distance from high to low tide mark too large for practical sampling.

Size of Sampling Zone

An area 6 meters (20 linear feet) along the beach and from backshore to low tide mark across the beach.

Frequency of Sampling

Every 9th and 10th days - In this way the 9th day sampling will represent 9 days of tar accumulation and the 10th day samplings will represent one day of tar accumulations.

Duration

One year, to commence at any time of the year.

Number of Samplings

Two sets - 35 samplings each (one set of 35 day 9; one set of 35 day 10).

Sampling Procedure

Stake out area. Clean off all debris from backshore to waterline prior to sampling. Sample only at or near time of low tide. Pick up all visible solid and semi-solid pieces of tar on surface of beach only. Weigh and record recoveries. The Workshop suggested some modifications to the format(s) as given in the Operational Plan for the Pilot Project and recommended that the Joint Task Team refine the reporting forms and include these incorporations in the final version of the Operational Plan for the Pilot Project.

PROCEDURES FOR SAMPLING AND REPORTING PETROLEUM HYDROCARBONS DISSOLVED AND DISPERSED IN SEA WATER

Co-Chairmen: Drs. E. Levy and M. Ehrhardt
Rapporteur : Dr. A. Zsolnay

Sampling

It has been agreed that, in the initial stage of the Pilot Project, water samples would be collected from one meter depths. Uncontaminated water samples are readily collected by the following method:

> 50 ml of hydrocarbon-free carbon tetrachloride[1] are placed in a clean[2] brown-glass bottle (3-4 litres). The bottle is sealed with a screw cap lined with degreased tin foil. This preparation should be carried out by the participating laboratory prior to the field work. Immediately before samples are taken, the bottle, with cap removed, is placed in the weighted holder (cf. Fig. 1).
>
> While the ship is still moving slowly forward, the assembly is thrown overboard from the bow and as far as possible away from the ship. The bottle will immediately sink and fill with water. Upon retrieval, some water is spilled (sufficient to allow for possible thermal expansion) out of the bottle. The cap is securely fastened and the bottle stored away.
>
> Caution: Throughout the procedure, great care must be taken to avoid contamination.

Frequency of sampling

Where possible, samples should be taken daily from ships in transit. From permanent stations, including Ocean Weather Ships, sampling should be done on a bi-weekly basis.

Recommendations

Recognizing that the immediate surface might be more important with respect to environmental processes, it is recommended that appropriate methods will be developed to sample surface films.

Recognizing that suitable procedures to collect water samples for low level hydrocarbon analyses from greater depths are not yet fully adequate, it is recommended that suitable sampling devices and procedures be developed.

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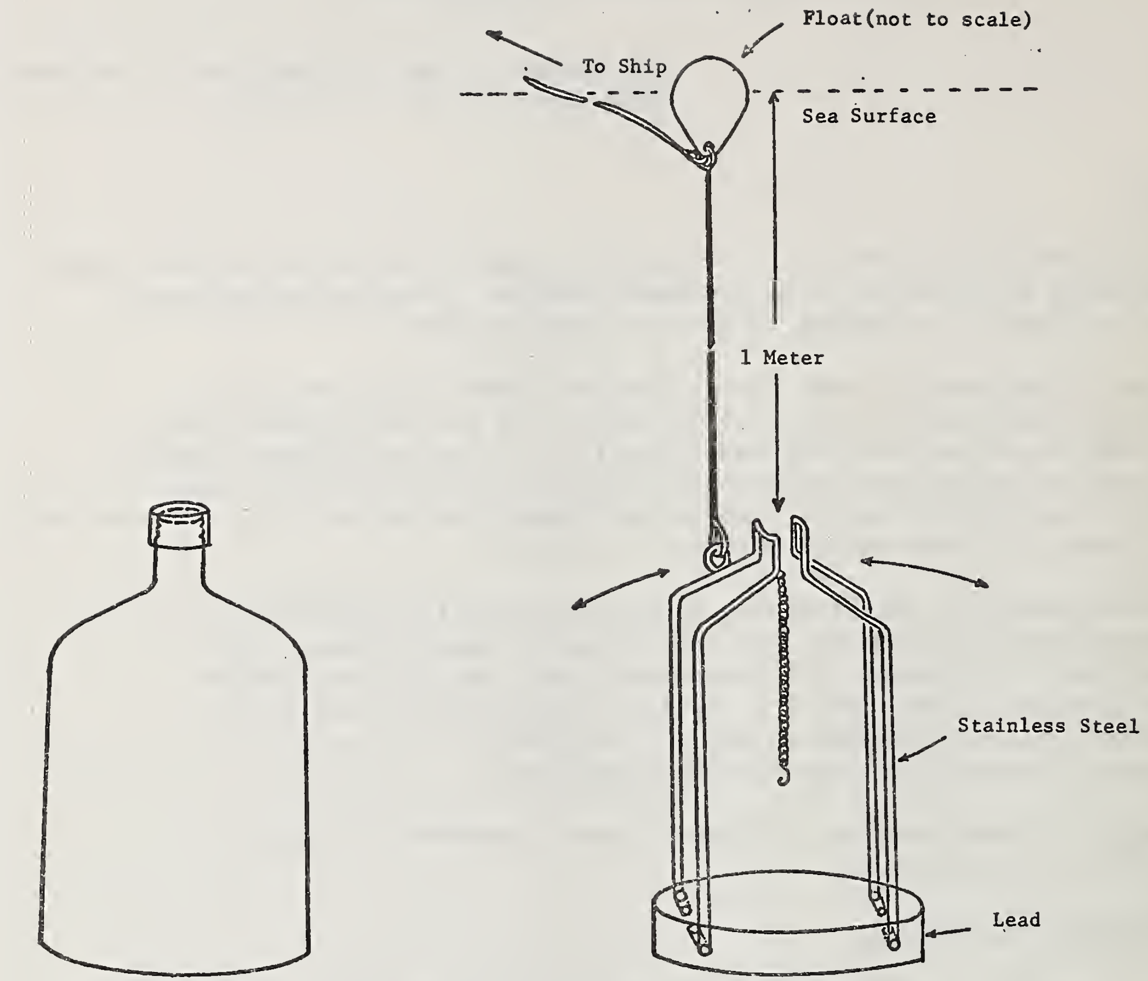
[1] or an appropriate amount of other suitable solvents; car should be exercised in the use and handling of carbon tetrachloride.

[2] hydrocarbon-free as determined by blanks



Sample Bottle with Cap

Bottle Holder with Floatation Unit

Figure 1.

DISSOLVED HYDROCARBON SAMPLING DEVICE

When taking a sample, the bottle cap is removed, the bottle is placed in the holder by swinging open the stainless steel cage, and the bottle is secured within the cage. The assembly is then thrown overboard from the bow, away from the ship but held by a retrieving line. After the bottle sinks and the sample is obtained, the bottle is hauled in, some water is spilled out of the bottle (to allow for possible thermal expansion), the cap is fastened and the bottle is labelled and stored away.

It is further recommended that methods be developed to collect samples from ships other than research vessels without interfering with their normal operations. For example, cartridges containing suitable absorbents may be placed in a by-pass to the sea water intake.

Sample Preservation

As carbon tetrachloride is an effective bacteriostat, further preservation of the samples is not necessary.

Recording of Samples

A log must be maintained to identify the samples, noting the position, date and time. Specified environmental data should also be given when possible. The Workshop suggested some modifications to the format(s) as given in the Operational Plan for the Pilot Project and recommended that the Joint Task Team refine the reporting forms and include these incorporations in the final version of the Operational Plan for the Pilot Project.

A label should be attached to the sample bottle bearing the sample number from the log and the position, date and time of the sample. This was to be designed by the Task Team for inclusion in the Operational Plan for the Pilot Project.

Dispatch of Samples

Sample bottles, together with the logs, should be packed securely in the transit case provided (to be determined nationally) and sent to the appropriate analysis laboratory.

Analysis Procedure

The Workshop decided to focus the quantitative analyses on aromatic hydrocarbons because:

(1) They are considered to have the greatest environmental impact in terms of toxicity;

(2) They seem to offer a means to differentiate between biogenic and petroleum derived hydrocarbons;

(3) Relatively straightforward and sensitive analytical methods exist for their estimation.

It is recommended, therefore, to use fluorescence spectrophotometry for quantitative measurements as described below:

Processing and analysis of samples

After shaking the water-CCl_4 mixture, allow the two phases to separate, pipet off the CCl_4[3] and place it in a clean glass bottle.

[3] Caution must be exercised in the use and handling of CCl_4.

Add 50 ml hydrocarbon-free CCl_4 to the seawater, carry out a second extraction and add CCl_4 to the previous 50 ml. Measure the volume of seawater processed.

Evaporate CCl_4 in a rotary evaporator or with mild heating on a hot plate (do not boil).

Prepare quantitative extract in n-hexane (5 ml clean volumetric flask).

Transfer to a 1 cm silica cell for fluorescence spectrophotometry.

Scan both excitation and fluorescence spectra. (Crude and residual fuel oils have excitation and fluorescence maxima in the neighborhood of 310 and 360 nanometer, respectively. The optimum wavelength for excitation and emission should be selected.)

The intensity of the fluorescence is measured and compared with a series of standard solutions[4] of similar composition and concentration under identical instrumental conditions.

Finally, calculate the concentration of oil present in water.

Ref: E. M. Levy, Water Research, 5, 723 (1971)

Alternative Methods

UV-absorption spectrophotometric measurement after column chromatographic clean-up and concentration (A. Zsolnay, Chemosphere, 6, 253-260, 1973).

Other analytical methods such as gas chromatography are not meant to be excluded. Indeed, gas chromatography provides much more information on the composition of samples, but it is not sufficiently sensitive for the concentrations expected to be encountered in other than highly polluted sea areas.

It is recommended that research be undertaken to develop and/or assess simple, fast, reliable and inexpensive methods for future stages of the Pilot Project.

Handling of Data

Data obtained from the analysis of water samples should be recorded on forms as developed by the Task Team for inclusion in the Operational Plan and the forms submitted through national channels as established by the National Coordinator, to the IGOSS "Responsible National Oceanographic Data Centers" (RNODC's). The WC IODE's ad hoc Group on IGOSS Data Archiving and Exchange, in conjunction with the ad hoc Group on Marine Pollution Data and the ad hoc Group on Format Development, should be instructed to prepare a supplement to the IGOSS Manual on Data Archiving and Exchange, outlining marine pollution data archival arrangements.

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[4] API Reference crude oil (medium aromatic content) is recommended as standard.

STANDARDS AND INTERCOMPARISON CRITERIA

Co-Chairmen: Drs. J. NcNesby and
R. Hiltabrand
Rapporteurs: Dr. R. Pierce and
Ms. S. Dyszel

This session indicated the feasibility of the use of reference petroleum samples; however, there is little, if any, information available on a standard petroleum reference material for marine environmental monitoring.

In order for any material to qualify as a reference material, the accuracy must be established by procedures such as those used for certification of standard reference materials by the U.S. National Bureau of Standards. These procedures may be obtained from the following reference:

> "Standard Reference Materials: The Role of SRM's in Measurement Systems by Cali, J.P., et al, NBS Special Publication 260-46 (in press), Gaithersburg, Maryland, USA."

A complete evaluation of the analytical method used must accompany the standard reference material before its reliability can be determined.

It is recommended, at this time, that (1) the American Petroleum Institute (API) reference samples be used as standard reference material; however, it is advisable that these samples undergo internal calibration by various laboratories as soon as possible and that this calibration be supervised by a central coordinating agency such as the U.S. National Bureau of Standards to establish the validity of the testing and the samples (these API samples can now be obtained through Dr. J. R. Gould, Secretary, American Petroleum Institute, 1801 K Street, N.W., Washington, D.C. 20006); (2) future research should investigate the "feasibility" of establishing other hydrocarbon standard material in:

(a) seawater
(b) sediments
(c) biological material

(the recommendations for specific standards in other materials depends upon the specific analytical procedures applied); (3) all reporting methods should be standardized; (4) the Systeme International d Unites (SI units) be used; (5) all intercomparisons should include reporting blanks with each set of analyses; and (6) multiple samples should be obtained from each sample site and analyzed when possible.

OIL IN MARINE ORGANISMS AND SEDIMENTS; SAMPLING AND ANALYTICAL METHODS

Co-Chairmen: Drs. F. Weiss and
J. Farrington
Rapporteur : Mr. R. Clark

General Comments on the Operational Plan

(1) The sampling and analysis of marine organisms and sediments are beyond the scope of the Pilot Project on Marine Pollution Monitoring under the framework of IGOSS.

Justification: This recommendation is made after consideration of the current state-of-the-art of analytical methods and data interpretation based on a broad evaluation of numerous scientific papers including the summaries of presentations at this symposium.

(2) However, we believe there are several suggestions that can be set forth for establishing future priorities for the use of marine organisms and sediments in petroleum pollution monitoring.

Recommendations

(1) Sampling

(a) We recommend the development of acceptable sampling methods. The sampling methods should be based on consultations between biologists, geologists, analytical chemists and geochemists. In order to avoid contamination of the samples, procedures such as those described by Grice, et al, (1972) should be used.

> Ref: Grice, G. D. Harvey, G. R.,Bowen, V. T. and Bacus, R. H., The Collection and Preservation of Open Ocean Marine Organisms for Pollutant Analysis, Bull. Envir. Contam. Toxicol. 7, 125-132 (1972).

(b) Once acceptable sampling methods have been developed, these methods should be employed wherever possible, to collect, sort, catalogue, preserve, and archive marine organism and sediment samples for future chemical analysis. Samples must be accompanied by adequate documentation.

(c) The development or choice of a suitable archiving program for biological and sediment samples can only be initiated after consultation with experts in this field, such as those of the Smithsonian Institution.

(2) Analysis

(a) The current methods of analysis for petroleum in marine organisms and sediments are still in a research mode with respect to applicability in an international monitoring program. This is especially apparent when considering monitoring in those areas where organisms and sediments may be expected to have low concentration levels, that is, on the order of 10^{-6} grams of petroleum per gram dry weight of sample.

(b) The presentations at this symposium as described in the summaries of papers contain many promising methods of analysis currently underway as part of national research programs. This research should be encouraged and the exchange of information and ideas should be channeled through IGOSS.

(c) Once methods applicable to monitoring programs have been developed, they may then be applied to the archived samples and to future sample collections.

Analytical Standards and Criteria

Refer to report on Standards and Intercomparison Criteria and the section below on Supporting Studies for Expansion and Further Development of the Pilot Project.

Data Handling

To be determined by future Workshops at such time as sampling for petroleum in sediments and marine organisms becomes a part of the Pilot Project. In the interim, data from research data will be reported and exchanged under the chemistry format as developed by the IOC WC for IODE.

Contents of Final Report on Pilot Project

With regard to one specific suggestion in the Joint IOC/WMO Planning Group for IGOSS document of October 1973 (IOC-WMO/IPLAN-II/3) on page 32 of Annex V, section b, item 8, concerning analysis of pollutants in fish meal and fish solubles, we would recommend that the analysis for petroleum not be considered during the Pilot Project. The analytical methods are not to a sufficient degree of standardization to permit a global monitoring of the world fish meal industries. In addition, low level petroleum contamination may be introduced during the processing of the fish meal. Thus, analysis would not provide a true assessment of natural conditions.

Supporting Studies for Expansion and Further Development of the Pilot Project

We would recommend that consideration be given to the convening of a future scientific workshop solely on the sampling and analysis of marine organisms and sediments and that this workshop be called in January 1976 to assess the state-of-the-art. If sufficient national or regional efforts have provided acceptable methods for sampling, analysis and data interpretation, a period of one year following this workshop should be provided for an intercalibration of methods between participating national centers under the designation of IGOSS. An evaluation of the sampling and analytical methods for petroleum in marine organisms and sediment should be presented at the end of the Pilot Project.

Should the opportunity arise, organisms collected during surface tar ball sampling tows (neuston net) should be separated from the tar balls and debris and preserved for future analysis. A complete description of the net tow sample must be included with the biological sample. Only excised tissue samples and organ samples should be analyzed when methods applicable to the monitoring program are developed since the exterior of the organisms will probably be subjected to contamination by petroleum in the neuston tows.

Technical Assistance Program Needs

Specific training and education programs in the areas of chemical oceanography, organic analytical chemistry and routine laboratory instrumentation and electronics should be encouraged in context of IGOSS, especially through some of the existing international development programs. We would recommend two levels of effort:

(1) A technical training program of 2-3 month duration to provide a practical training session for field and laboratory technicians at an existing petroleum pollution monitoring laboratory, such as the Bermuda Biological Station for Research. The first aspects of these training sessions should be initiated no later than six months after the start of the Pilot Project.

(2) Exchange of field and laboratory-level working scientists between existing petroleum pollution monitoring laboratories and those national research centers wishing to develop a capability for such monitoring efforts. The duration of each exchange would vary with the individual scientist but would probably be for a period of two months to 4 years. This program should be initiated immediately after the start of the Pilot Project.

ASSESSMENT OF BIOLOGICAL EFFECTS OF PETROLEUM HYDROCARBON POLLUTION

Chairman: Mr. M. Stansby
Rapporteur: Dr. T. Joyner

Methodology

This session dealt with matters which are not directly concerned with monitoring, per se. The monitoring will not in any case deal directly with biological assessments, so we are not commenting on biological assessment methods. We feel, however, that the methods to be used in the Pilot Project and in subsequent extensions of such work should receive input from this session to indicate types of monitoring information which would be most useful to research attempting to evaluate effects of petroleum hydrocarbons upon the biota. This topic was considered in the paper by Dr. La Roche and it made up a large part of the discussion following the paper in this session. It was also discussed in Mr. Stansby's paper during the final session on May 15: Biological Environmental Effects.

During discussions at another session, the possibility was brought up of sampling surface water films during the forthcoming Pilot Project. The taking of such samples would be extremely advantageous for research worker's information. It is realized that it would probably be impractical to adopt such sampling routinely, for the upcoming Pilot Project. It is recommended, however, that if even a small part of the samples could be taken in this way, this should be considered. Even should this be impossible, we strongly recommend that ways to do this be considered for future projects. We know that devices have been used in the past for collecting thin films at the surface in the open ocean. A device employing a rotating cylinder mounted in a wood frame which allowed it to be operated in somewhat rough seas, was built and used at Scripps Institution of Oceanography, a few years ago.

Since the primary concern about oil pollution in the ocean is its impact on living resources and human health, means for monitoring the effects of petroleum oils on these resources and their products that are used as items of human diet must be developed. These should include the selection of appropriate marine organisms, collecting, preserving, shipping and processing of samples as well as the development of appropriate analytical techniques. For the selection and sampling of appropriate marine organisms, it is suggested that particular attention be paid to the sea-atmosphere and sea-sediment interfaces where, because of the natural concentration of initially dispersed pollutants on these surfaces, the greatest contamination of organisms can be expected to occur. Examples would be the contamination of the eggs and larvae of pelagic fish and zooplankton and of unicellular marine plants at the sea-air interface by thin films of oily pollutants, and the contamination of the benthic fauna that form the basic food of bottom fish by oily pollutants absorbed onto settling particles.

Supporting Studies for Expansion and Further Development of the Pilot Project

Responding to the request of the IOC/WMO Task Team on the Marine Pollution Monitoring Pilot Project (8-10 May, 1974) that the Workshop consider such methods of marine pollution monitoring as analysis of pollutants in fish meal from the world fish meal industries, we recommend that the participating States, in their national marine research programs, be encouraged to undertake development of appropriate methods for sampling and analyzing fish, destined for the production of fish meal, for components of petroleum oils that could adversely affect the palatability or safety as foodstuffs of fish meal products. As these methods are developed and standardized, they could be considered for future inclusion in an expanded pollution monitoring program.

We recommend that research be pursued toward developing methods for sampling marine organisms, especially fin fish, in such a way that subsequent analysis of the resulting sample would give hydrocarbon values predictive of potential harm to the fish. This could probably be achieved by finding parts (organs or tissues) of the fish where the hydrocarbons were present in such a way that they either were in a position in close proximity to vulnerable sites within the fish or could be readily mobilized into such position. Present practice of analyzing whole fish results in including hydrocarbons often detoxified in fatty areas or sometimes even the inclusion of hydrocarbons in feed in the digestive tract which would never or only partially be laid down in the tissue of the fish.

Biological Indicators and Accumulators for Marine Pollution Monitoring (Surveillance)

The report of the Third Session of the IOC Group of Experts on Oceanographic Research as it relates to IGOSS was reviewed where reference is made to the use of biological indicators and accumulators as a means for marine pollution monitoring; (Document SC-IOC/IRES-III/3, Annex IV refers.)

The term "bioassay" as used in paragraph 2 of Item 7 of the Report is open to conflicting interpretations. If used in the sense of using biological organisms to indicate the effects of pollution on the life processes of the organism (as in the case of laboratory mice), then we do not believe that it could be effectively applied to pollution monitoring on a global scale. The range of interfering effects on the organism from environmental parameters other than those being monitored would be too great to permit precise interpretation of observed effects.

If used in the sense of indicating the presence or absence of a pollutant by its physical accumulation on the organism, then the selection and testing of the suitability of organisms adequate to specific geographic areas of interest to the Pilot Project should be encouraged by the participating Member States. When such bioassay systems are sufficiently developed they can be proposed by the member states for inclusion in the Pilot Project.

Technical Assistance Program Needs

Use should be made of national laboratories possessing expertise in monitoring and other analytical procedures including biological assessment. When program needs require assistance in any of these fields it should be possible to arrange for trainees to be stationed for limited periods of time at such laboratories to enable them to acquire experience in the technique desired. For example, there are several laboratories in the United States, especially on the Pacific Coast, experienced in biological assessment techniques involving petroleum oil which could assist in such work for a limited number of trainees.

WORKSHOP CONCLUSIONS AND RECOMMENDATIONS ON DATA HANDLING

Co-Chairmen: Mr. R. Morse and Mr. T. Winterfeld

Data Handling

The Workshop recognizes the importance of making data and information resulting from the pollution monitoring programs routinely available on an international basis.

The Workshop reaffirms the previous recommendations of planners of IGOSS-affiliated projects that, on the subjects of data (recording data formats, data exchange and archival mechanisms and procedures, inventories and data documentation), specific advice and guidance would be sought from the IOC WC on International Oceanographic Data Exchange (IODE).

Forms for visual observations of oil slicks and other floating pollutants, and for sampling and reporting of particulate petroleum residues, and for the results of analyses of dissolved/dispersed oil, should be submitted through national channels, as already established under the WC IODE (in accordance with procedures to be included in the IOC Manual on IGOSS Data Archiving and Exchange), to the IGOSS "Responsible National Oceanographic Data Centers" (RNODC's).

Recommendations

(1) All participants in the Pilot Project should be made aware of and urged to complete and submit, in timely fashion, the IOC first-level inventory, ROSCOP (Report of Observations/Samples Collected by Oceanographic Programs).

(2) The WC IODE's *ad hoc* Group on Marine Pollution Data Exchange, in collaboration with the *ad hoc* Group on IGOSS Data Archiving and Exchange and the *ad hoc* Group on Format Development, is requested to review the data formats and procedures of IPLAN-II as modified by this Workshop, and develop appropriate guidelines for the reporting, inventorying, documenting and international exchange of marine pollution data as a supplement to the IGOSS Manual on Data Archiving and Exchange.

(3) The WC IODE's *ad hoc* Group on Marine Pollution Data Exchange should accelerate its efforts to develop inventory and documentation procedures for marine pollution data and place priority in this development upon petroleum hydrocarbon data, so as to minimize the variability of local or national reporting formats in use at the commencement of the Pilot Project.

(4) All marine pollution (chemistry) data and information, whether or not suitable for centralized archiving and routine exchange, should be inventoried and fully documented (see Annex I) and incorporated into a centralized international referral system as is being developed by the IODE *ad hoc* Group on Marine Pollution Data Exchange and the Joint Task Team (IOC, ICES, IAEA, FAO, IHO, WMO, WHO, IMCO, UNEP) on Interdisciplinary and Interorganizational Data and Information Management and Referral (IMAR).

(5) Any samples obtained under this Pilot Project, which are to be stored for future chemical analysis should be accompanied by documentation at the same level of detail as is being prescribed for actual data and inventories of data (see 3 and 4 above).

Minimum General Documentation to Accompany Marine Chemical, Biochemical and Geochemical Data and Inventories

(NOTE; This documentation is to supplement that required)
(by the basic Data Documentation Form (DDF) which pro-)
(vides for time, position, cruise number, name of institu-)
(tion and scientist, related meteorological data, etc.)

Sampling Documentation

	Water	Biological	Sediment
Salinity	X	X	
Temperature	X	X	
Bottom Depth	X	X	X
Sampling Apparatus	X	X	X
Filtered/Unfiltered	X		
Filter Specs.	X		
Hydro Cable (Type, Condition, Greased?)	T,O	T,O	
Species		X	
Sex		X	
Weight		X	
Length		X	
Dissection Procedure		X	
Tissue		X	
% Moisture		X	
% Organic Matter			X
Size Fraction			X
Mineralogy			X

	Water	Biological	Sediment
Depth in Core			X

Storage Documentation

	Water	Biological	Sediment
Type Container	X	X	X
Reagents Added	X	X	X
Storage (Frozen, etc.)	X	X	X
Length of Storage	X	X	X

Sample Preparation Documentation

Sample Split	X	X	X
Extraction Procedure	X	X	X
Concentration Procedure	X	X	X
Digestion Technique		X	X
Sample Purification	X	X	X
Lab Sample ID No.	X	X	X

Analysis Documentation

Date of Analysis	X	X	X
Analytical Method*			
Make & Type of Instrument	X	X	X
Number & Concentration Range of Calibration Standards	X	X	X
Blank Value	X	X	X
Precision	X	X	X
Estimated Accuracy	X	X	X
Basis of Rept. Data (Wet, Dry, etc.)	X	X	X

	Water	Biological	Sediment
Units of Measurement	X	X	X
No. of Replicate Analyses	X	X	X
Confirmation by Other Technique	P	P	P
PCB Analysis - Yes/No? (in Conjunction with DDT)	P	P	P

Legend

P = Pesticides

T = Trace Elements

X = All Samples

O = Organics

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*Each specific analytical technique requires additional documentation related to that technique; i.e., gas chromatography, mass spectroscopy, UV flourescence, neutron activation analysis, etc. ATTACH SEPARATE SHEET.

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MARINE POLLUTION MONITORING (PETROLEUM) SYMPOSIUM AND WORKSHOP

National Bureau of Standards
Gaithersburg, Maryland
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